ANA EMANDI

BASIC INORGANIC CHEMISTRY

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Referenți științifici: Prof. dr. **Elena Cristurean**
Prof. dr. **Maria Negoiu**

Biblioteca Centrală Universitară
" Carol I " Bucureşti
Cota IV 521 280

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Şos. Panduri, 90-92, Bucureşti - 76235; Telefon/Fax: 410.23.84
E-mail: editura@unibuc.ro
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CHAPTER I
MATTER AND ENERGY

I.1CHEMISTRY

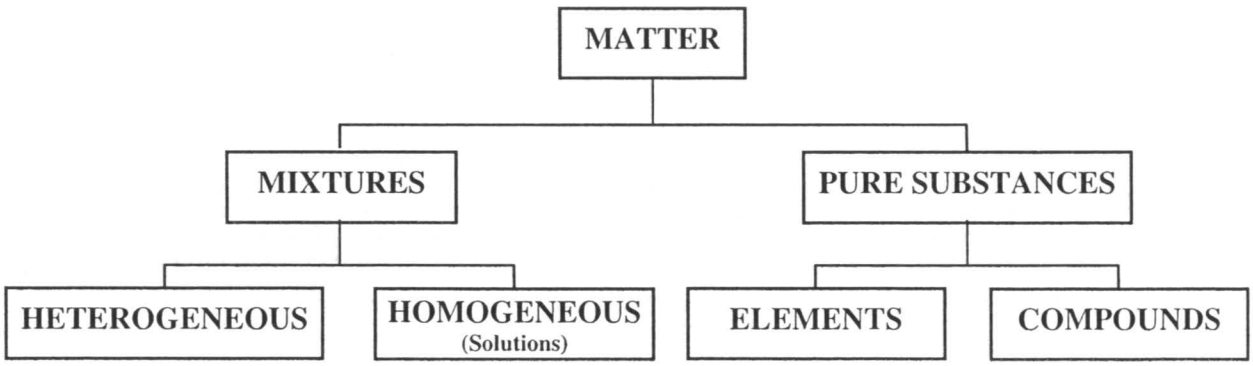
I. Definition: Chemistry is the study of the composition of substances, the changes they undergo, and our attempts to control or modify them.

II. Sub visions of Chemistry:

1. General Chemistry presents a broad outline of the subject as a whole. General and basic laws and principles are emphasized. Considerable descriptive material is usually included.
2. Analytical Chemistry is concerned with a study of kids and amounts of various elements and compounds that are present in matter.
3. Organic Chemistry deals with products that contain carbon, and emphasizes a study of plant and animal products.
4. Physical Chemistry deals with the general principles of scientific laws that underlie transformations of matter.
5. Biological Chemistry deals with the chemistry of living processes.
6. Food Chemistry, Colloid Chemistry, Chemical Engineering, Paint Chemistry, Water Chemistry, Carbohydrate Chemistry, cover the fields suggested by their titles.
7. Matter and Energy

I.2 MATTER

Matter is anything that occupies space and has mass. It can change its form and characteristics.



States of Matter

Matter can be divided into three main categories, liquids, solids and gases. These are called the three states of matter and are sometimes referred to as phases at constant temperature.

Substance: ensemble of particles, which establish interactions between them. A substance has typical properties that cannot be attributed to the structural submicroscopic unities from which it is composed.

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Pure substance is the substance that is composed from the same type of particles.(structural unities).

Mixtures are systems formed by two or more substances, which do not react between them.
Ex: Molecules of nitrogen, molecules of oxygen, and particles with different nature form the air.

Homogeneous system is a material system formed from a single phase in which the component substance or the component substances are not separated by separating surfaces.

Heterogeneous system is a material system composed by many phases and in which the phases are separated by delimitating surfaces.

Elements

An element is a simple substance that cannot be separated into simpler substances by ordinary chemical means. There are109 known chemical elements. They may be classified into two main types: metals and nonmetals. Few elements are found in the pure state, such as iron, lead, silver and copper. Most of the others are founded in various combinations with other elements in forms called compounds.
Elements are composed of atoms containing an equal number of positive charges, protons in the nucleus and negative charges, electrons in orbit. The molecules also contain a neutral particle, which has no electrical charge, a neutron.
The nuclear charge is equal to the number of positive charges, the number of protons, and this number is called the atomic number of the element. (Z)

$$E_Z^A$$

The mass of the atom equals the sum of the masses of the protons and neutrons. The sum of the masses of the protons and neutrons is called the atomic mass. (A)
Isotopes are spices of atoms of the same chemical element that have the same atomic number but different atomic mass number.

$$U_{92}^{235} \qquad U_{92}^{238}$$

Compounds

Chemical combinations of two or more different elements form the chemical compounds. These compounds may be decomposed into their constituent elements by chemical means. There are over 300000 known compounds prepared in laboratory or extracted from natural sources.
Chemical compounds are characterized by always having homogeneity, a constant composition and definite chemical and physical properties.

Ex: - the water is a compound substance formed from hydrogen and oxygen and the properties of water are quite different from those of its constituent elements.

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Changes in Matter: Physical or Chemical

I. Physical changes.

a) Physical changes alter only the physical properties of a substance and not the chemical properties.
b) The composition remains the same and the original properties can usually be restored by simple means.
c) The original substance retains its identity.

Ex: The freezing of water, the breaking of a glass, and the grinding of sugar are examples of physical change.

II. Chemical changes.

a) Chemical changes alter the properties, and particularly the chemical properties, so completely that there results an entirely new substance.

Ex: The burning of oil the rusting of iron, and the fermentation of fruit juices are examples of chemical changes.

b) There are fundamentally five types of chemical change.

Ex: I. Chemical Combination is the direct combination of two or more elements or compounds to form more complex compounds.
- Iron combines with oxygen to form iron rust.

II. Decomposition is the breaking down of a compound into two or more substances.
- Water decomposes into its two constituent elements, hydrogen and oxygen by electrolysis.

III. Displacement is when a free element displaces another element in a compound.
- An iron nail displaces copper from a solution of copper sulfate.

IV. Double Decomposition is when two compounds react with each other to give two new compounds.
- Sodium hydroxide (household lye) reacts with hydrochloric acid (muriatic acid) to produce sodium chloride (common salt) and water.

V. Internal Rearrangement is when the atoms within a molecule rearrange to give a different compound without the loss or gain of any atoms.
- Ammonium cyanate, when heated, produces urea.

Properties of Matter: Physical or Chemical

A chemist most often identifies an unknown substance by measuring its properties and comparing them to the properties recorded in the chemical literature for the known substance.

I. Physical Properties

Color – Sulfur is yellow.
Odor – Ammonia has a sharp odor.
Taste – Sugar is sweet.
Specific gravity – Lead is heavy aluminum is light.
Hardness – Chromium is hard.
Electrical conductivity – Copper is high.
Heat conductivity – Aluminum is high.

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Melting point – Carbon is extremely high.
Tensile strength – Iron and steel are high.
Ductility – Silver is unusually ductile.
Malleability – Gold is unusually malleable.

More commonly, we measure the physical properties of elements or compounds. These are properties that can be measured without changing the chemical identity of a substance.
For example: Density = mass per unit volume, that is, grams per cubic centimeter;
Specific gravity = the density relative to an accepted standard, usually water for liquids and solids, and air for gases; Solubility; Melting Point and Boiling point.

For liquids and gases, density can be found in a straightforward way by measuring, independently the mass and the volume of a sample, for solids is a bit more difficult, because their volume are found indirectly.

Melting Point, Boiling Point.
The melting point is the temperature at which a substance changes from the solid to the liquid state. If the substance is pure the temperature stays constant during melting. For a pure substance the melting point is identically with the freezing point.

Ex: Ice melts at 0 degrees and pure water freezes at the same temperature.
The boiling point of a liquid is the temperature at which bubbles filled with vapor from within the liquid.

Solubility
Solubility is measured with the number of grams of the substance that dissolves in 100g of solvent at a given temperature.

Ex: At 20^0 C ~32g of KNO_3 dissolves in 100g of H_2O .

Most mixtures can be separated into their components using the difference in physical properties of the components.

Ex: Differences in melting point gives the distillation method and differences in solubility gives fractional crystallization.

A major task of chemistry is to separate the components of mixtures. The most widely used separation technique in chemistry today is chromatography – column C

- High-pressure liquid chromatography
- Paper C (HPLC)
- Thin layer C (TLC)

II Chemical Properties

Stability toward heat.
Quicklime, CaO, is stabile toward heat while mercuric oxide, HgO, is easily decomposed with heat.

Resistance to reaction when brought into contact with other substances.
Ex: Iron rusts readily in contact with air while gold does not.

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I.3 ENERGY

Introduction.

1. Energy is the ability to do work.
2. All transformations of matter are accompanied by transformations of energy.
3. Energy cannot be created or destroyed (First Law of Thermodynamics or Law of Energy). Energy may be changed from one to another.

Types of Energy

1. Potential energy is the energy a body possesses by virtue of its position.
2. Kinetic energy is energy due to motion.
3. Radiant energy is the energy of radiation and may be visible (light) or invisible.
4. Chemical energy is the energy that is stored or released when chemical transformations take place.
5. Electrical energy is the energy of moving electrons due to difference in the electrostatic pressure.
6. Thermal energy is the energy of heat and is measured in calories.
7. Atomic energy is the energy obtained as a result of loss in mass occurring in certain types of nuclear transformations.

I.4 SYMBOLS, FORMULAE AND EQUATIONS

Introduction

In any O level course you must have used chemical symbols and formulae. You will also have written chemical equations and used them in simple calculations of quantities required for reaction. I make no apology for covering this work again and in detail. When marking A level scripts it is surprising how many elementary mistakes involving symbols, formulae and equations are seen.

Symbols and formulae

A symbol-either a capital letter alone or a capital letter and a small letter represent each element. The complete list of symbols can be reference to the Periodic Table

Each compound is represented by a formula, which gives the proportions of the different elements it contains.

Ex: 24 g of magnesium combines with 16 g of oxygen in every 40 g sample of magnesium oxide. The formula is MgO, showing that 1 mole of magnesium atoms (24 g) combines with 1 mole of oxygen atoms (16 g).

The formula of many compounds can be use of the list of ions in Table

Table - Common ions

Positive ions	Negative ions
lithium Li^+	fluoride F^-
sodium Na^+	chloride Cl^-
potassium K^+	bromide Br^-
silver Ag^+	iodide I^-
copper(II) Cu^{2+}	hydroxide OH^-
lead(II) Pb^{2+}	nitrate NO_3^- (nitrate(V))

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magnesium Mg^{2+}	nitrite NO_2^- (nitrate(III))
calcium Ca^{2+}	carbonate CO_3^{2-}
strontium Sr^{2+}	hydrogen carbonate HCO_3^-
barium Ba^{2+}	sulphate SO_4^{2-} (sulphate(VI))
zinc Zn^{2+}	hydrogensulphate HSO_4^-
aluminum Al^{3+}	sulphite SO_3^{2-} (sulphate(IV))
iron(II) Fe^{2+}	oxide O^{2-}
iron(III) Fe^{3+}	sulphide S^{2-}
chromium(III) Cr^{3+}	phosphate PO_4^{3-} (phosphate(V))
manganese(II) Mn^{2+}	manganate(VII) MnO_4^-
cobalt(II) Co^{2+}	ethanedioate $C_2O_4^{2-}$
nickel(II) Ni^{2+}	chlorate(V) ClO_3^-
ammonium NH_4^+	chlorate(I) OCl^-
hydrogen H^+	chromate(VI) CrO_4^{2-}
	dichromate(VI) $Cr_2O_7^{2-}$

In forming the compound, the number of ions used is such that the number of positive charges equals the number of negative charges. For example, sodium chloride is made up from Na^+ and Cl^- ions. Since a sodium ion has a single positive charge and chloride ion has a single negative charge, the formula of sodium chloride is NaCl. Sodium sulphate is made up from Na^+ and SO_4^{2-} ions. Twice as many sodium ions as sulphate ions are necessary in order to have equal positive numbers of positive and negative charges. The formula is Na_2SO_4. Chromium (III) sulphate is made up from Cr^{3+} and SO_4^{2-} ions and its formula is $Cr_2(SO_4)_3$. Table contains further examples.

Table Finding the formula

Compound	Ions present		Formula
copper(II) oxide	Cu^{2+}	O^{2-}	CuO
ammonium chloride	NH_4^+	SO_4^{2-}	$(NH_4)_2SO_4$
potassium manganate(VII)	K^+	MnO_4^-	$KMnO_4$
calcium ethanedioate	Ca^{2+}	$C_2O_4^{2-}$	CaC_2O_4
chromium(III) oxide	Cr^{3+}	O^{2-}	Cr_2O_3
hydrochloric acid	H^+	Cl^-	Hcl
nitric acid	H^+	NO_3^-	HNO_3
sulphuric acid	H^+	SO_4^{2-}	H_2SO_4

All of the compounds above are composed of ions. Many compounds are not ionized. The formulae of some of these compounds are shown in Table .

Table Some compounds not composed of ions

Compound	Formula	Compound	Formula
Water	H_2O	Sulphur dioxide	SO_2
Carbon dioxide	CO_2	Sulphur(VI) oxide	SO_3
Carbon monoxide	CO	Ammonia	NH_3
Nitrogen monoxide	NO	Hydrogen chloride	HCl
Nitrogen dioxide	NO_2	Methane	CH_4

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I.5 FORMULAS

Definition

The composition of a compound is represented by a chemical formula, which is made up of the symbols of all the elements present in the compound. We can use a suitable subscript if more than one atom of a single element is present in the molecule.

Derivation of Formulas

From known groups and valences

For most inorganic compounds the algebraic sum of all positive and negative valences is equal to zero.

From percentage composition where molecular weight is known.

Ex: an organic compound has an approximate molecular weight of 46 and the following percentage composition: C 52.2% , H 13% , and O 34.8%. Calculate its formula.

C 46*0.522=24.0 ;24.0:12=2

H 46*0.130=5.98 ;5.98:1~6

O 46*0.348=15.9 ;15.9:16~1

Therefore, the formula of this compound is: C_2H_6O.

From percentage composition only.

Divide the percentages by the respective atomic weights of each element present.

Reduce these values to the simplest ratios

This gives the simplest possible formula and does not necessarily coincide with the true M.F.

Ex: A compound contains 1.26%H, 38.78%P, 59.96%O. What is its simplest possible formula? Hat are some other possible formulas?

H 1.26 :1=1.26

P 38.78:31=1.25

O59.96:16=3.77

Therefore, the simplest formula is: HPO_3, other possible formulas:$H_2P_2O_6$; $H_3P_3O_9$

-

I.6 NOMENCLATURE OF INORGANIC COMPOUNDS

Binary compounds

a) *Binary Acids*: are distinguished by the prefix "**HYDRO"** and the ending "**ic**"

HCN	**HYDRO** cyan**ic** acid
HCl	hydrochloric acid
HI	hydro iodic acid
H_2S	hydro sulfuric acid

b) *Salts*: involve a metallic cation and a nonmetallic anion. Name the metal, abbreviate the nonmetallic and in end name with "-**ide**"

BaF_2	barium floride
NaCl	sodium chloride
LiH	lithium hydride
CaO	calcium oxide

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MgI_2 magnesium iodide
K_2S potassium sulfide

The prefixes "mono", "di", "tri" etc are not used with metals in group first and second because they do not show variable valence.

c) *Metals with variable valence*: the ending "ous" denotes the lower oxidation state (valence or combining power) of the metal, "ic" the higher oxidation state.

HgO mercuric oxide
Hg_2O mercurous oxide
$FeCl_3$ ferric chloride
$FeCl_2$ ferrous chloride

The stock system, which designates the oxidation state of the metal with a roman numeral. This system is especially useful here the metal has more than two oxidation states and the "ous" and "ic" system is inadequate:

VCl_2 vanadium II chloride
VCl_3 vanadium III chloride
VCl_4 vanadium IV chloride
VCl_5 vanadium V chloride

Covalent compounds involve two nonmetallic elements. Use the appropriate Greek prefixes "mono-di-tri-tetra-penta" to indicate the number of atoms of each element involved.

CO_2 carbon dioxide
PCl_3 phosphorous tri-chloride
Cl_2O dichloride monoxide
N_2O_4 dinitrogen tetroxide

Cyanide Radicals: These radicals, a group of atoms, two or more, usually act as one unit in a reaction. Use the ending "ide".

NH_4CN ammonium cyanide
NH_4Cl ammonium chloride
Na OH sodium hydroxide
$Ca(OH)_2$ calcium hydroxide
KCN potassium cyanide
$Fe(OH)_3$ ferric hydroxide

Trivial Names:

H_2O water;
NH_3 ammonia;
PH_3 phosphine;
AsH_3 arsine;
CH_4 methane;
C_2H_6 ethane.

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Polyprotic Acids: contains more than one replaceable hydrogen. Anhydrides react with water to produce the ORTHO acids on Hydration. The ortho acids form "phyro " or "meta" acids, by dehydratation.

Ortho, Pyro, Meta, Acids:

H_3PO_4 orthophosphoric acid
HPO_3 meta phosphorious acid
$H_4P_2O_7$ pyro phosphoric acid
H_3PO_3 ortho phosphorous acid
HPO_2 meta phosphorous acid
$H_4P_2O_5$ pyro phosphoric acid

Salts of Polypro tic Acids: are formed when one or more of the hydrogen ions are replaced by metal ions. The first name given is usually preferred:

$NaHCO_3$ sodium bicarbonate, sodium acid carbonate, sodium hydrogen carbonate
NaH_2PO_4 monosodium phosphate, primary sodium phosphate
Na_2HPO_4 disodium phosphate, secondary sodium phosphate

I.7 CHEMICAL EQUATIONS

Chemical equations are widely used in textbooks an examination paper. An equation is a useful summary of a chemical reaction, and it is always theoretically possible to obtain the equation from the results of an experiment. It is advisable to be able to write equations in your answers to A level questions. You should write any relevant equation even if you are not directly asked to do so.

The steps in writing a chemical equation are as follows:

(i) Write down the equation as a word equation using either the information given or your memory. Include all reacting substances (reactants) and all products (do not forget small molecules such as water) e.g.

calcium hydroxide + hydrochloric acid → calcium chloride + water

(ii) Fill in the correct formulae for all the reacting substances and products.

$$Ca(OH)_2 + HCl \rightarrow CaCl_2 + H_2O$$

(iii) Now balance the equations. During a chemical reaction, atoms cannot be created or destroyed (Law of conservation of mass). There must be the same total numbers of the different atoms before and after the reaction. When balancing an equation only the proportions of the reacting substances and products can be altered-not the formulae.

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$$

In organic chemistry the equations can be more complex. Frequently, in the interest of clarity, the formulae are drawn out as structural formulae to show clearly the changes that have taken place. Also, less emphasis may be given to balancing the equation. You should however balance the equation if possible.

For example, the reaction between bromoethane and a solution of potassium hydroxide in ethanol can be written.

$$CH_3CH_2Br \xrightarrow{HBr} C_2H_4$$

It is better to write

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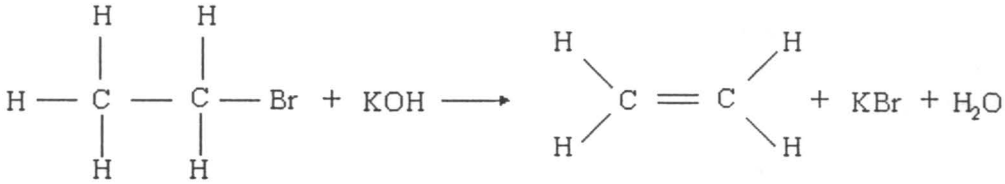

bromoethane ethene

The equation is balanced and shows clearly the change taking place *i.e.* elimination of Hbr.

(iv) Finally, the states of reacting substances and products can be included in small brackets after the formulae.

(s) for solid (sometimes (c) is seen for crystalline solid)
(l) for liquid
(g) for gas
(aq) for a solution with water as solvent

These state symbols may not be required and may not give you extra credit from the examiner but they do help your thinking considerably and give a good impression.

$$Ca(OH)_2\ (aq) + 2HCl\ (aq) \rightarrow CaCl_2\ (aq) + 2H_2O\ (l)$$

In the interests of simplicity of this text, state symbols are not included throughout the book, unless considered important.

Information provided by an equation

$$CaCO_3\ (s) + 2HCl\ (aq) \rightarrow CaCl_2\ (aq) + CO_2\ (g) + H_2O\ (l)$$

This equation gives the following information: 1 mole of calcium carbonate reacts with 2 moles of hydrochloric acid to produce 1 mole of calcium chloride, 1 mole of carbon dioxide and 1 mole of water. The equation also gives the states of all reactants and products.

In general, a chemical equation gives:

(i) the chemicals reacting together and the chemicals produced,

(ii) the physical states of reactants and products, and

(i) the quantities of chemicals reacting together and produced.

The equation does not, however, give information about energy changes, the feasibility of reaction, the rate of reaction or the conditions necessary for reaction to take place.

At O level you will have attempted calculations of quantities of chemicals reacting. For example, using the above equation and the relative atomic masses (H = 1, C = 12, O = 16, Cl = 35.5, Ca = 40), calculate the mass of solid calcium chloride, which could be produced, from 20g of calcium carbonate.

From the equation, 1 mole of calcium carbonate ($CaCO_3$) produces 1 mole of calcium chloride ($CaCl_2$)

$40 + 12 + (3 \times 16)$g $CaCO_3$ produces $40 + (35.5 \times 2)$g $CaCl_2$

100g $CaCO_3$ produces 111g $CaCl_2$

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$$20\text{g } CaCO_3 \text{ produces } \frac{111}{100} \times 20\text{g } CaCl_2$$
$$= 22.2\text{g of } CaCl_2$$

You will attempt similar questions at A level. In some cases, for example when considering carbon dioxide as a product, it is more useful to measure the volume of gas produced. This can then be converted into numbers of moles of carbon dioxide by using the information (given on the examination paper) that 1 mole of any gas occupies 22 400 cm^3 at standard temperature and pressure, stp. If the volume is measured at conditions other than stp, and it usually is, it is necessary to convert the volume measured to the volume the gas would occupy at stp (273 K and 101.3 kPa) using the equation:

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

For example, what mass of calcium carbonate would react with dilute hydrochloric acid to produce 133.5 cm^3 of carbon dioxide at 27°C and 100 kPa.

Volume of carbon dioxide at stp = V_1 cm^3

$$\frac{V_1 \times 101.3}{273} = \frac{133.5 \times 100}{(273+27)}$$

$$V_1 = \frac{133.5 \times 100 \times 273}{101.3 \times 300} = 120\ cm^3$$

From the equation,

100g of calcium carbonate (1 mole) produces 22 400 cm^3 CO_2 at stp

$\frac{100 \times 120}{22\,400}$ g of calcium carbonate produces 120 cm^3 CO_2 at stp

Mass of calcium carbonate = 0.54g

Calculation of percentage yield

In organic chemistry, a 100% conversion of reactants into products is rarely achieved. From an equation it is possible to calculate a theoretical yield, *i.e.* the mass that would be produced if a 100% conversion were achieved. If you are given the actual mass produced, it is possible to calculate the percentage yield by:

$$\text{Percentage yield} = \frac{\text{mass obtained}}{\text{theoretical yield}} \times 100$$

Example: Propan-2-ol reacts with iodine and sodium hydroxide on warming to produce triiodomethane. In an experiment a student obtained 39g of triiodomethane from 10g of propan-2-ol. What was the percentage yield? (H = 1, C = 12, O = 16, Na = 23, I = 127).

$CH_3CH(OH)CH_3 + 4\ I_2 + 6\ NaOH \rightarrow CHI_3 + CH_3COONa + 5\ NaI + 5\ H_2O$

Mass of 1 mole of propan-2-ol = (12 × 3) + 8 + 16g = 60g

Mass of 1 mole of triiodomethane = 12 + 1 + (3 × 127) = 394g

From 60g of propan-2-ol, 394g of triiodomethane would be produced if 100% conversion.

Theoretical mass of triiodomethane from 10g propan-2-ol = $\frac{394}{6}$ g = 65.66g

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$$\text{Percentage yield} = \frac{39}{65.66} \times 100 = 59.4\%$$

Ionic equations

You may well have written ionic equation at O level but they become much more significant at A level. Ionic equations are useful because they emphasize the important changes taking place in a chemical reaction.

Taking the reaction between acidified potassium manganate (VII) and iron (II) sulphate as an example. The full equation is:

$$2\ KMnO_4 + 8\ H_2SO_4 + 10\ FeSO_4 \rightarrow 2\ MnSO_4 + 8\ H_2O + 5\ Fe_2(SO_4)_3 + K_2SO_4$$

In this equation there are a number of ions, which take no part in the chemistry; they are present before and after the reaction. These tend to confuse the change taking place and can often be ignored.

Expanding the equation to show the ions present.

$$2(K^+MnO_4^-) + 8(2H^+SO_4^{2-}) + 10(Fe^{2+}SO_4^{2-}) \rightarrow 2(Mn^{2+}SO_4^{2-}) + 8H_2O + 5(2Fe^{3+}3SO_4^{2-}) + 2K^+SO_4^{2-}$$

Cross out ions appearing on both sides of equation

$$2MnO_4^- + 16H^+ + 10Fe^{2+} \rightarrow 2Mn^{2+} + 8H_2O + 10Fe^{3+}$$

The equation can be divided through by 2 to give the simplest equation.

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

The represents the simplest ionic equation for this reaction. The equation must be balanced in the usual way with equal numbers of each type of atom on left and right hand sides. In addition, the algebraic sum of the charges on the left hand side equals that of the right hand side.

In the example,

$$\text{LHS } (-) + 8(+) + 5(2+) = 17(+)$$
$$\text{RHS } (2+) + 4(0) + 5(3+) = 17(+)$$

The ionic equation can be broken down into 2 half equations which added together produce the overall equation.

(i) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

(ii) $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

Equation *(i)* represents the equation of manganese (VII) to manganese (II). Equation *(ii)* represents the oxidation of iron (II) to iron (III).

I.8 BASIC LAWS OF CHEMISTRY

1.The **Law of Conservation of mass**. This law was first stated by the French chemist Antoine Lavoisier in 1789.In modern form ,it says *that there is no detectable change in mass in an ordinary chemical reaction*. If atoms are "conserved" in a reaction (Postulate 2 above), mass will also be conserved.

Lavoisier has often been referred to as the "father of modern chemistry". He was among the first to carry out quantitative chemical experiments and draw logical conclusions from them. His experiments demonstrating the conservation of mass were described in the first modern textbook of chemistry, which he published in 1789.Five years later, at the age of 50,Lavoisier died on the guillotine, a victim of hysteria that accompanied the French Revolution.

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2.The **Law of Constant Composition**. This tells us that *a compound always contains the same elements in the same proportions by mass*. If the atom ratio of the elements in a compound is fixed (Postulate 3), their proportions by mass must also be fixed. The validity of this became generally recognized at about the same time that Dalton's theory appeared. Prior to 1808 many people agreed with the French chemist Berthollet. He believed that the composition of a compound could vary over wide limits; depending on haw it was prepared.

3.The third postulate of the atomic theory is in many ways the most important. Among other things, it led Dalton to formulate the **Law of Multiple Proportions**. This law applies to the situation in which two elements form more than one compound. It states that, in these compounds *the masses of one element that combine with a fixed mass of the second element are in a ratio of small whole numbers*. To derive the La of Multiple Proportions, Dalton reasoned along the following lines: Suppose elements A and B form two different compounds .In one of these (AB), one atom of A might be combined with one atom of B. The second compound (AB_2) might contain two atoms of B per atom of A. If this is true, the mass of B combined with a fixed mass of (such as one gram) of A would be twice as great in the second compound. In other words, the masses of B per gram of A in the two compounds would be in a 2:1 ratio.

Despite the successes of Dalton's atomic theory, it was not immediately accepted by all scientists. In particular, many chemists felt it was a waste of time to speculate on the particulate nature of matter.

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The Atomic Theory

The notion that matter consists of discrete particles first appears in the writings of Democritus, a Greek philosopher. His teacher, Leucippus, has introduced him to it. Plato and Aristotle rejected the idea. For nearly two thousand years, the concept of the atom remained just that, an abstract idea divorced from experimental reality.

In 1808, an English schoolteacher and amateur meteorologist, John Dalton, developed an atomic model of matter that offered a simple explanation of several of the laws of chemistry. Three of the main postulates of modern atomic theory, all of which came from Dalton, are given below.

1.*An element is composed of tiny particles called atoms. All atoms of a given element show the same chemical properties.* The element oxygen is made up of oxygen atoms. These atoms are much too small to be seen or weighed directly. All oxygen atoms behave chemically in the same way.

2.*Atoms of different elements have different properties. In an ordinary chemically reaction, no atom of any element disappears or is changed into an atom of another element.* The chemical behavior of oxygen atoms is different from that of hydrogen atoms or atoms of any other element. When hydrogen and oxygen react, all the hydrogen and oxygen that react are present in the water formed. No atoms of any other element are formed.

3.*Compounds are formed when atoms of two or more elements combine. In a given compound, the relative numbers of atoms of each kind are different and constant. In general, these relative numbers can be expressed as integers or simple fractions.* In the compound water, hydrogen atoms and oxygen atoms are combined with each other. For every oxygen atom present, there are always two hydrogen atoms.

The atomic theory explains three of the basic laws of chemistry.

1.The Law of Conservation of Mass.

The law of conservation of mass was discovered by M.V. Lomonosov in 1748 and experimentally proved by A.L. Lavoisier in 1774.

Lavoisier pointed out that: all the changes that takes place in nature are produced in such a way that as much it is taken from one element, it is added to another. In modern form, it says that *there is no detectable change in mass in an ordinary chemical reaction.* If atoms are "conversed" in a reaction, mass will also be conserved.

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Lavoisier has often been referred to as the "father of modern chemistry". He was among the first to carry out quantitative chemical experiments and draw logical conclusions from them. His experiments demonstrating the conservation of mass were described in the first modern textbook of chemistry, which he published in 1789.

2.The Law of Constant Composition.

This tells us that *a compound always contains the same elements in the same proportions by mass.* If the atom ratio of the elements in a compound is fixed, their proportions by mass must also be fixed.

The validity of this law became generally recognized at about the same time that Dalton's theory appeared. Prior to 1808 many people agreed with the French chemist Berthollet. He believed that the composition of a compound could vary over wide limits, depending on how it was prepared. Joseph Proust refuted Berthollet by showing that the "compounds" Berthollet had cited were actually mixtures.

It is known that in certain compounds, particularly metal oxides and sulfides, the atom ratio may vary slightly from a whole number ratio. Careful analyses of samples of nickel oxide prepared by heating nickel with oxygen at high temperatures give an atom ratio of 0.97 : 1.00 rather than the expected 1 : 1 ratio. Compounds of this type are sometimes referred to as "Berthollides" or, more frequently, nonstoichiometric compounds. The derivations from constant composition arise because of defects in the crystal structure.

3.The Law of Multiple Proportions.

This law applies to the situation in which two elements form more than one compound. It states that, in these compounds *the masses of one element that combine with a fixed mass of the second element are in ratio of small whole numbers.* This law was deduced by Dalton. Suppose elements A and B form two different compounds. In one of these (AB), one atom of A might be combined with one atom of B. The second compound (AB_2) might contain two atoms of B per atom of A. If this is true, the mass of B combined with a fixed mass (such as one gram) of A would be twice as great in the second compound. In another words, the masses of B per gram of A in the compounds would be in a 2 : 1 ratio.

In water, the ratio between the hydrogen mass combined with the oxygen is 1/8. One gram of hydrogen is combined with 8 grams of oxygen forming 9 grams of water. An excess of hydrogen or oxygen in the reaction mixture remains uncombined. One gram of hydrogen is combined with 16 grams of sulph in the hydrogen sulfide, with 3 grams of carbon in methane, with 35.5 grams of chlorine in hydrochloric acid etc. On the other hand, 8 grams of oxygen are combined with 8 grams of sulph in the sulph dioxide, with 7 grams of nitrogen in the nitrogen oxide, with 12 grams of magnesium in the magnesium oxide etc.

Some elements form, between them more then one combination, in different mass ratios, but always corresponding to integer and small numbers (*the multiple proportion law*). For example:

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	Nitrogen : oxygen ratio
N_2O	14 : 8
NO	14 : 16
N_2O_3	14 : 24
N_2O_4	14 : 32
N_2O_5	14 : 40

The simplest explanation of these facts, and of many similar ones, is that the elements are composed from very small particles called atoms and in a chemical reaction, the atoms of one element combined with the atoms of the other element (Dalton, 1805). If the water had composed with one atom of hydrogen and one atom of oxygen, corresponding to the chemical formula HO, the mass of an atom of oxygen would be eight times heavier then the mass of the hydrogen atom. If the hydrogen sulfide would have the composition HS, then the mass of one sulph atom would be 16 times bigger then the mass of the hydrogen atom, etc. From the analysis of a great number of substances containing hydrogen and another element, it was observed that hydrogen atom mass is the smallest from the atomic masses of the other elements. This conclusion proved to be correct. The hydrogen atom mass was taken as unity atomic mass. The formulas HO, HS and others were not correct; the ratio between the combining masses of the elements is not always an atomic mass ratio. So, it is made the distinction between the chemical equivalent mass and the atomic mass of an element.

It is called the *chemical equivalent* of an element, that quantity, in grams, from an element, which is combined with one gram of hydrogen, or with eight grams of oxygen.

If the chemical combinations between two elements composed by the atoms A and B would have always the composition AB and if A would be hydrogen or oxygen, then the chemical equivalent of B would be equal with the *atomic relative mass* of the element B (on a scale in which the mass unity is equal with the mass of a hydrogen atom).

But things are more complicated then that. It is quite known that the hydrogen forms with oxygen, except of water, another combination, hydrogen peroxide, in the ration H/O = 1/16. The carbon forms with oxygen two oxides, one in which the ratio O/C is equal with 8/6 (carbon oxide) and another one, which has the ratio 8/3 (carbon dioxide). The nitrogen forms with oxygen five different oxides (N_2O, NO, N_2O_3, N_2O_4, N_2O_5), with the nitrogen equivalents (grams of nitrogen bounded by 8 grams of oxygen) are: 14, 7, 4.67, 3.5 and 2.8.

In conclusion, the atoms of two elements, A and B, doesn't form just combinations of the type A_1B_1, but can also form combinations of the type A_1B_2, A_1B_3, A_1B_4, A_2B_1, A_2B_2, A_2B_3, A_2B_4, A_2B_5, A_3B_1, A_3B_2, etc. When an element forms more then one combinations with hydrogen or oxygen (or with another element) *its' atomic mass is equal with one of its equivalents or with a multiple of it.*

One of the fundamental methods for determining which chemical equivalent of an element corresponds to its' atomic mass is based on the reactions in gaseous state.

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Gas Combination Laws.

Constant volume law

When a combination is formed by the reaction between two elements in gaseous state or when gas is formed by the decomposition of a combination, the volumes of these gases (measured in the same conditions of temperature and pressure) are in integer and small ratios (Gay–Lussac, 1808).

To the formation of hydrochloric acid, one volume of hydrogen reacts with an equal volume of chlorine; to the formation or the hydrolysis of water, the ratio of the hydrogen/oxygen volumes is 2/1; at the synthesis or at the decomposition of ammonia, the volume ratio hydrogen/nitrogen is 3/1. A lot of examples confirm this law of the constant volumes for the reactions involving gases.

Constant volume law is based on the 'ideal gas' state (at low pressure and at a temperature more above the boiling temperature). In those gases, the spaces between the component particles of the gases are extremely large in rapport to the particle dimensions. The particles are so small in comparison with the total gas volume that these can be considered as being material points, which doesn't interact except by the elastic clashes. It is stated that, in the same conditions of temperature and pressure, *equal volumes of gases (ideal gases) contain an equal number of particles.*

The simplest representation that it can be made about the component particles of gaseous elements is that these are singular atoms. If this hypothesis would be true, at the combination of a volume of hydrogen with one volume of chlorine it should result one volume of hydrochloric acid. At the combination of two volumes of hydrogen with one volume of oxygen it should result one volume of water vapors and at the combination of three volumes of hydrogen with one volume of nitrogen it should result one volume of ammonia. The experiment gives different results:

Hydrogen + Chlorine = Hydrochloric acid
1 vol. 1 vol. 2 vol.
Hydrogen + Oxygen = Water (vapors)
2 vol. 1 vol. 2 vol.
Hydrogen + Nitrogen = Ammonia
3 vol. 1 vol. 2 vol.

Avogadro's law.

In 1811, Avogadro stated that the smallest particles in the gaseous elements, like hydrogen, chlorine, oxygen and nitrogen, are not atoms but molecules composed by two atoms: H_2, Cl_2, O_2 and N_2. In this case, the reaction between the hydrogen and the chlorine can be written as:

$$n\,H_2 + n\,Cl_2 = 2n\,HCl$$
1 vol. 1 vol. 2 vol.

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where n is the number of molecules contained in a given volume of gas. If is simplified by n:

$$H_2 + Cl_2 = 2\ HCl$$
$$1\ vol.\quad 1\ vol.\quad 2\ vol.$$

The same is for:

$$2\ H_2 + O_2 = 2\ H_2O\ (vapors)$$
$$2\ vol.\quad 1\ vol.\quad 2\ vol.$$
$$3\ H_2 + N_2 = 2\ NH_3$$
$$1\ vol.\quad 1\ vol.\quad 2\ vol.$$

In consequences, after Avogadro, *equal volumes of gases, at the same temperature and pressure, contain an equal number of molecules.*

An important consequence of this fact is that the molecules of hydrochloric acid are composed by an atom of hydrogen and another of chlorine, of water by two atoms of hydrogen and one of oxygen and of ammonia by three atoms of hydrogen and one of nitrogen.

From the Avogardo's law it results a relation that allows the determination of molecular masses.

Ideal Gas Laws

The Ideal Gas State is represented by the mathematical relations between the pressure, volume and temperature (Boyle, Mariotte, Charles, Gay–Lussac, Regnault, Kelvin and others in the XVIIth, XVIIIth and XIXth century).

3.1. *Volume–Pressure Relation*

At constant temperature, the gas volume is inverse proportional with the pressure (Boyle–Mariotte law). By noting the volume by v and the pressure by p:

$$p\ v = \text{constant.}$$

A gas that follows the Boyle–Mariotte law, at any temperature and pressure, it is called a perfect or an ideal gas. When, for a gas, the temperature is higher and the pressure is lower, this gas is closer to a perfect gas label.

An Ideal Gas is called a gas that satisfies completely some mathematical equations:

$$p\ v = \text{constant.}$$
$$v = c\ T\ \text{(at constant pressure)}$$

called the *ideal gas laws*.

3.2. *Volume and Pressure Variation versus Temperature*

A gas, heated or cooled, at constant pressure, is diluted, respectively, is contracted. The volume is proportional with the temperature, as is seen in the following relationship:

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$$v = c\,(t^{o} + 273)$$

Where v is the volume of a given quantity of gas and t^{o} is the temperature in Celsius degrees. If is noted v_o the volume occupied by a gas at 0°C, it is obtained the relation: $c = v_o/273$. This is followed by the next sentence: *when, at constant pressure, the temperature of gas varies with one degree, the gas volume varies with 1/273 from the gas volume at 0°C.*

Another equation can be written using the *absolute temperature*, T:

$$T^{o} = 273.15 + t^{o}.$$

The absolute zero point is –273.15° and is noted by 0°K*. Usually, it is admitted that there can not be temperatures lower then 0°K. So, the volume variation can be written as:

$$v = c\,T \text{ (at constant pressure)}$$

At constant pressure, volume of a gas varies directly proportional with the absolute temperature (Gay–Lussac law).

In a similar way, it was proven experimentally that, for a gas with constant volume, the temperature variation with one degree determines a variation of the pressure with 1/273 towards the gas pressure at 0°C. So, at constant volume, the gas pressure varies directly proportional with the absolute temperature (Charles law):

$$p = c\,T \text{ (at constant volume)}$$

3.3. *Volume – Pressure – Temperature Relationship*

The most general case of the transformation of the ideal gas is the one where all the three state parameters variates The relationship between them is realized with the help of the perfect gas state equation which is a result of the combination of the Boyle–Mariotte, Gay–Lussac and Charles laws:

$$p\,T = p_o\,T_o\,(1 + \alpha t^{o})$$

where $\alpha = 1/273.15$ and $t^{o} = T - 273.15$.

$$p\,v\,/\,T = \text{cons.}$$

From this relation it results that the three physical magnitudes that characterize a given mass of gas, the volume, temperature and pressure are interdependent.

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* In the honor of W. Thomson (Lord Kelvin).

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3.4. *Molar Volume. Mole.*

Taking into account the Avogadro's theory, the elemental gaseous molecules, like hydrogen, chlorine, oxygen and nitrogen, are composed by two atoms and have the formulas: H_2, Cl_2, O_2, N_2. On the other hand, from all the elements, hydrogen has the smallest chemical equivalent. It can be considered as the mass unity, the relative atomic mass of the hydrogen equal to 1. So, the relative molecular mass of hydrogen is 2.

The *mole* is a quantity, from a substance, expressed in grams and equal to the absolute mass sum of the N particles, represented by a chemical formula (N being the Avogadro number). A mole of hydrogen is (approximately) equal with 2 grams of hydrogen.

It is called a *molar volume*, V, the volume occupied by one mole from a substance. One mole of substance occupies, in *normal conditions* (at the temperature 0°V and at the pressure 1 atm = 760 mm Hg = 760 torr), a volume of 22.4 liters. In a general expression, this can be said as: *the molar volumes of ideal gases, at constant temperature and pressure, are equal*. Those are independent of the chemical nature of the substances. In normal conditions (0°C; 1 atm), the molar volume of an ideal gas, V_o, is:

$$V_o = 22.415 \text{ liters.}$$

The fact that a great number of gases, different by their chemical nature have, in normal conditions, the same molar volume, V_o, this can be the basis of a molecular mass determination method. It is evidently that the mass of an ideal gas volume of 22.4 liters is equal to the molecular mass of the substance. So, the molecular mass of oxygen is 32, etc.

3.5. *Ideal Gas State Equation*

For a mole of gas, it can be written:

$$p\,V = R\,T.$$

Here, V is the volume occupied by an ideal gas at the absolute temperature T and pressure p (in atm). When the temperature is T = 0°C = 273.15°K and the pressure is one atmosphere, it can be calculated the value of the proportionality constant R:

$$R = \frac{1 \times 22.415}{273.15} = 0.08206 \text{ L} \cdot \text{atm} \cdot \text{grad}^{-1} \cdot \text{mole}^{-1}$$

$$p\,V = 0.08206\,T.$$

The ideal gas constant is an universal constant.

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3.6. *Partial Pressure Law* (Dalton)

The partial pressure of every component of a mixture of gases is proportional to the volume fraction occupied by the component.

The (dry) air is a mixture of three principal gases with the volume proportions: 78% nitrogen, 21% oxygen and 1% argon. The partial pressure of these gases, at 1 atm is:

$$p_{N2} = 0.78 \text{ atm} \qquad p_{O2} = 0.21 \text{ atm} \qquad p_{Ar} = 0.01 \text{ atm}.$$

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CHAPTER III
ATOMIC MASS. MOLECULAR MASS. DETERMINATION METHODS

III.1. **Atomic Mass**

With a mass spectrometer we can determine the atomic mass of each isotope of an element.

The atomic mass of an element tells us how heavy, on the average, an atom of that element is compared to an atom of another element. The atomic mass scale is based on the most common isotope of carbon, C–12 atom, which is assigned a mass of exactly 12 atomic mass units (a.m.u.):

mass C–12 atom = 12 a.m.u. (exactly)

Hydrogen has an atomic mass of 1.00794 a.m.u., so the hydrogen atom is about 1/12 as heavy as a C–12 atom:

$$\frac{\text{mass H atom}}{\text{mass C–12 atom}} = \frac{1.00794 \text{ a.m.u.}}{12 \text{ a.m.u.}} = 0.0839950$$

In the general case, for two elements X and Y:

$$\frac{\text{mass of an atom of Y}}{\text{mass of an atom of X}} = \frac{\text{atomic mass of Y}}{\text{atomic mass of X}}$$

The atomic mass of an element is a weighted average of the atomic masses of its individual isotopes, taking into account their relative abundance:

the percentage of the several isotopes must add up to 100;

$$\%\text{ of } Y_1 + \%\text{ of } Y_2 + \cdots = 100\ \%.$$

Ex:

$$\begin{array}{ll} {}^{12}_{6}C & {}^{13}_{6}C \\ 99.9\ \% & 1.1\ \%. \end{array}$$

$$\text{(a.m.u.) } C = \frac{1.1}{100} \cdot 13 + \frac{99.9}{100} \cdot 12 = 12.01$$

the accuracy of tabulated atomic masses is limited by variation in natural abundance.

S is an interesting case. It consists largely of two isotopes: ${}^{32}_{16}S$, ${}^{34}_{16}S$. The abundance of the isotope 34 varies from about 4.18 % in sulfur deposits in Texas and Louisiana to 4.34 % in volcanic sulfur from Italy. This leads to an uncertainty of 0.006 a.m.u. in the atomic mass of sulfur.

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Determining the Atomic Weights by Chemical Methods

1.*From Molecular Weights and Percentage Composition.*

The atomic weight of an element is the greatest common divisor of members giving the weight of this element in one mole of each of a large number of its compounds.

The determination of the atomic mass of carbon from the molecular masses of some of its' combinations:

Combination	Carbon's equivalent	Molecular mass	Grams of Carbon Contained in one mole of combination	Formula	Atomic mass
Methane	3	16	12	CH_4	
Ethane	4	30	24	C_2H_6	
Ethylene	6	28	24	C_2H_4	
Acetylene	12	26	24	C_2H_2	12
Benzene	12	78	72	C_6H_6	
Carbon oxide	6	28	12	CO	
Carbon dioxide	3	44	12	CO_2	

In this way it can be concluded that the atomic weight of Carbon is 12.

2. *Rule of Dulong and Petit*

In 1819, in France, Dulong and Petit found, for solid elements, that the product between the atomic mass and the specific heat is constant:

atomic mass x specific heat = 6.4 cal/atom–gram · grad (= 26 J · $grad^{-1}$ · mol^{-1}).

For example: the iron specific heat is 0.111:

$$\text{atomic mass of iron} = \frac{6.4}{0.111} \approx 58.$$

One of the iron's equivalents is 28. The atomic mass of iron is twice as big as its' equivalent, approximately 56. Gold's equivalent in gold chloride is 65.65. Applying the Dulong and Petit law, it was found that the atomic mass is approximately 206. The closest multiple is 3 x 65.65 = 196.95. This is the exact value of the atomic mass.

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The Dulong and Petit's law is applied only to the solid elements with atomic masses bigger then 35. Those are almost all metals. Lighter nonmetals, like the two solid elements, which have small atomic masses, boron and carbon, give great errors.

3.*The Average of the Atomic Weight of Adjacent Elements*

The atomic weight of an element should be near the average of the atomic weights of elements occupying adjacent positions in the periodic table.

For example:

$$\begin{array}{ccc} {}_{10}\text{Ne} & {}_{11}\text{Na} & {}_{12}\text{Mg} \\ (20{,}183) & \downarrow & (24.312) \end{array}$$

average = 22.248

real = 22.9 .

4.*The Positive Ray Method*

The positive ray method, as perfected by the English physicist, F. W. Aston, will indicate the relative masses of different isotopes with an accuracy of 10^{-3} %.

5.*Using Equivalent Weights and Valance*

The equivalent weight of an element is the number, which represents the amount of the element that can react or remove 1 gram of hydrogen or 8 grams of oxygen.

Equivalents Law:

A chemical equivalent gives the ratio between;

$$\frac{m_H}{m_E} = \frac{E_H}{E_E}$$

1 g is E. W. of H

8 g O is E. W. of O

Generally:

$$E_{element} = \frac{A.W.}{Valance}$$

Valance: is the number of H atoms bonded or removed by an element, in a compound.

Oxidation State (o.s.): gives the ionic charge of an element in a compound regarding its electronegativity and when all electrons are shared.

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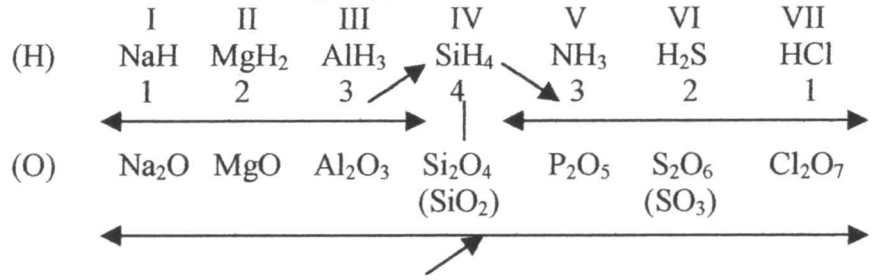
The valance in the main groups:



The oxidation states can be computed by knowing:

H —— o.s. +1 in nonmetallic compounds;

—— o.s. –1 in metallic compounds;

O —— o.s. –2 in all the compounds, except:

—— o.s. –1 in peroxides.

uncombined elements have the o.s. = 0.

in ionic compounds, the o.s. = the charge of ions.

in covalent compounds, the o.s. can be computed as an algebraic sum of all atoms for a natural compound.

$K_2Cr_2O_7$ ionic compound: $2K^+ Cr_2O_7^{2-}$

$o.s._K = +1$

$o.s._O = -2$

$o.s._{Cr} = ?$

$2 \cdot (+1) + 2 \cdot x + 7 \cdot (-2) = 0$

$2 \cdot x = 14 - 2$

$2 \cdot x = 12$

$x = +6$

Coordination Number (C.N.): is the number of direct neighbors around an atom or in a lattice or in a complex compound.

C.N. ~ 12, 8, 6, 4, 2.

Example: in NaCl lattice: $6\ Na^+$ $6\ Cl^-$

$C.N._{Na^+} = 6.$

coordination compound $[Cu(NH_3)_4]SO_4$

$C.N._{Cu^{2+}} = 4.$

Chemical Equivalents:

$$E_{oxid} = \frac{\text{M. M.}}{\text{the least common multiple between index of O and E}}$$

$$E_{Al2O3} = \frac{\text{M. M.}}{2 \times 3}$$

$$E_{CaO} = \frac{\text{M. M.}}{2}$$

(Ca_2O_2)

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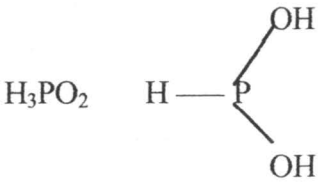
$$E_{HnA} = \frac{\text{M. M.}}{\text{n ionisable protons (or directly bonded by oxygen)}}$$

$$H_3PO_4 + Mg(OH)_2 \rightarrow MgH_2PO_4 + 2H_2O$$

$$E_{H3PO4} = \frac{\text{M. M.}}{3} \quad \text{(uncombined)}$$



H_3PO_2

$$E = \frac{\text{M. M.}}{2} \quad \text{(uncombined)}$$

$$E_{redox} = \frac{\text{M. M.}}{\text{no. of } e^- \text{ changed in reaction}}$$

This equivalent weights method is used for normal solutions. Is determined for compounds by comparing with the equivalent weight of a known compound.

The constant proportion law states the existence of some simple mass ratios between the elements in a compound. These ratios were called chemical equivalents. In the terms of the atomic theory, the chemical equivalents represent the relative masses of atoms that are combined in rapport to the hydrogen atom mass, the lightest of atoms.

The chemical equivalents can be determined with great precision through quantitative chemical analysis. According to the multiple proportion law, many elements have, in their different combinations, different equivalents. Only one of its' equivalents or an integer multiple of it can be equal to the atomic mass of the element.

6.Mass Spectrometer

The properties of positive ions allow the exact determination of their masses with the help of mass spectrometers.

In the scheme bellow is presented a mass spectrometer. A gas such as helium, at very low pressures, is bombarded by high–energy electrons, A few helium atoms are converted to He^+ ions. These ions are focused into a narrow beam and accelerated by a voltage of 500 to 2000 V toward a magnetic field. The field deflects the ion beam out of its straight line path, toward the collector.

For ions of a given charge, for instance +1, the extent of deflection depends upon the mass of the ion. The heavier the ion, the less it will be deflected. At a given magnetic field strength and accelerating voltage (V_1), a $^{12}C^+$ ion might arrive at point A (in the figure). Under the same conditions, $^4He^+$ ions might be deflected to point B.

The mass spectrometer. A beam of gaseous ions is deflected in the magnetic field toward the collector plate. Light ions are deflected more than heavy ones. By

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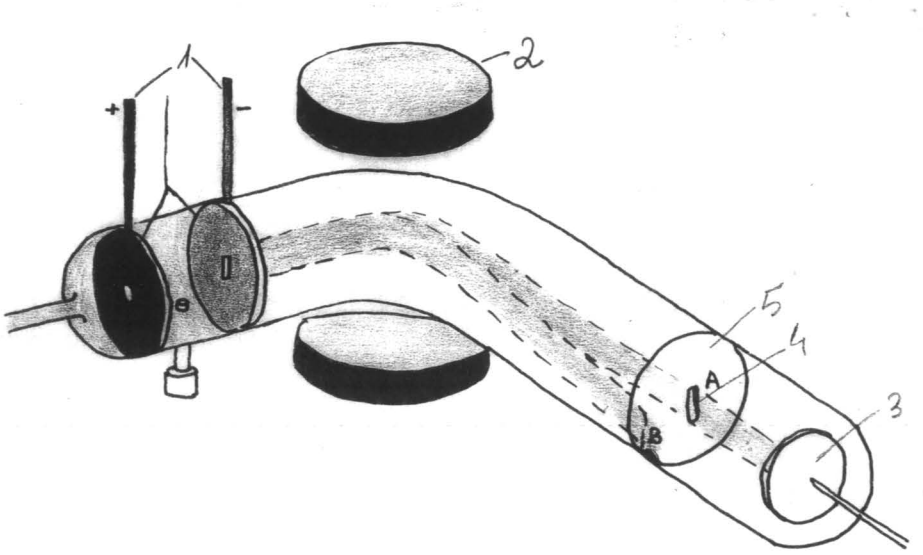
comparing the accelerating voltages required to bring the two ions to the same point, it is possible to determine the relative masses of the ions.

(1)–accelerating plates; (2)–magnet; (3)–Collector; (4)–slit; (5)–detector.

A–beam of $^{12}C^{+}$ ions, B–beam of $^{4}He^{+}$ ions.



Are called isotopes the atomic species belonging to the same element, differing by their mass but resembling very much by their physical and chemical properties. Because of the high resembling of the properties, isotopes of the same element can be separated very difficult, by special methods.

The existence of isotopes was first observed at the radioactive elements. With the mass spectroscopy it was proved that also common elements have isotopes, but not all.

Atomic masses of isotopes have numerical values very close to integer numbers (a little bit smaller or higher). So, to every isotope it is attributed a mass number denoted by *A*.

While the mass spectroscopy determines the mass (and abundance) of every isotope from a mixed element, the chemical method leads to average values of atomic masses. Important is the fact that the percentage (abundance) of isotopes in mixed elements is the same (with a few exceptions). For instance chlorine, which has an atomic mass of 35.453 (equal with the chemical equivalent), is a mixture of isotopes with the mass numbers A = 35 and A = 37 in proportion of 3 : 1. This can be the cause for the fact that some elements do not have atomic masses equal to integer numbers.

In nature, hydrogen is a mixture of isotopes with the mass numbers 1 and 2 in proportion of approximately 5500 atoms ^{1}H to 1 atom ^{2}H. The isotope ^{2}H is called deuterium (D) and ^{1}H is called protonium. Oxygen is a mixture of isotopes: ^{16}O : ^{17}O : ^{18}O in proportion of 3150 : 1 : 5; nitrogen is a mixture of ^{14}N (99.6%) with (0.4%); carbon is a mixture of ^{12}C (98.9%) with ^{13}C (1.1%).

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III.2. **Molecular Weight**

The molecular weight of a compound is the number of times its molecule is as heavy as one sixteenth part of the oxygen atom. It is also the sum of the atomic weights of all the atoms.

The Determination of Molecular Weight

A.Gases

Vapor Density Method

a. *Hydrogen Standard*: since hydrogen has a molecular weight of 2, the molecular weight of the other gases may be determined by multiplying their vapor densities related to hydrogen, by 2:

$$d_{N2/H2} = 14 \qquad M.\ M_{N2} = 14 \times 2 = 28.$$

The equation of the state of ideal gas is the basis of some methods for the determination of molecular mass of some substances in gaseous state.

If: n – the number of moles of gas $\qquad n = \frac{m}{M}$

m – grams of substance

M – the molecular mass of the substance

The equation: pV = R T is true for a mole of gas. For n moles of gas, the equation becomes:

$$p\upsilon = n\,R\,T$$

By replacing n, this becomes:

$$p\upsilon = \frac{R\,T\,m}{M}$$

By isolating M, it is obtained:

$$M = \frac{R\,T\,m}{p\upsilon}$$

or, if the density is d = m/υ:

$$M = \frac{R\,T}{P}\,d$$

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For a mole of gas, it can be written:

$$p\,V = R\,T.$$

Here, V is the volume occupied by an ideal gas at the absolute temperature T and pressure p (in atm). When the temperature is $T = 0^{\circ}C = 273.15^{\circ}K$ and the pressure is one atmosphere, it can be calculated the value of the proportionality constant R:

$$R = \frac{1 \times 22.415}{273.15} = 0.08206\ L \cdot atm \cdot grad^{-1} \cdot mole^{-1}$$

Knowing the constant R (in liter–atmospheres) and determining experimentally the volume v of a substance with the mass m (in grams) at the absolute temperature t and the pressure p (in atmospheres) it can be applied the formula: $M = RTm/(pv)$. On the other hand, if it is determined the gas density d at the absolute temperature T and the pressure p, it can be applied the equation: $M = RTd/p$. If it is determined the gas density d at $0^{\circ}C$ ($= 273^{\circ}K$) and pressure $p = 1$ atm, then:

$$M = 22.4\ d^{\circ}.$$

This method can be also applied to the molecular mass determination of solid and liquid substances if these can be transformed into gases or vapors. Because the equation is true only for ideal gases, the molecular masses determined this way differ from those real because of the different behavior of the gases or vapors resulted from the ideal gas behavior.

b. *Avogadro's Hypothesis Method*

The molecular weight of a gas is numerically equal to the weight in grams of 22.4 L of a gas measured in normal conditions ($0^{0}C$, 1 atm).

Example:

$$1\ L\ O_2 \rightarrow 1.429\ g$$
$$22.4\ L \cdot 1.429\ g = M.\ M._{O2} = 32$$

The easiest is the case of gaseous elements composed by two atoms (related to the Avogadro hypothesis) like H_2, O_2, N_2, Cl_2, Br_2 and I_2. For these elements, their atomic mass is equal to half of the measured molecular mass. The measured molecular masses of hydrogen, oxygen and nitrogen are approximately 2, 32 and 28. The atomic masses of these elements can also be approximated to 1, 16 and 14. (The exact atomic masses being those deduced from the chemical equivalents).

By using the density that was obtained experimentally:

$$\rho_{gas}^{absolute} = \frac{M.\ M.}{V_M}$$

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Because of the relative density, it can be found that:

$$d_{1/2}^{relative} = \frac{M_1}{M_2} = \frac{m_1}{m_2}$$

$$M_1 = d_{1/2} \cdot M_2$$

This method was applied also for the solid elements that can not be vaporized easily. In this case there was determined the molecular masses of some combinations of the element. The smallest quantity, in grams, contained in one mole of one of the elements' combinations is numerically equal to the atomic mass of the element. This is the case for the determination of the atomic mass of carbon.

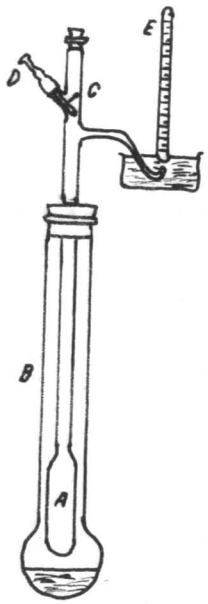
B.Liquids

1. One of the methods for the determination of the molecular mass of a volatile liquid compound is the heating at a temperature above the boiling point and the molecular mass is the weight in grams of 22.4 L of vapors (in normal conditions).

2. Victor Meyer Method (1878)

This method is used at the determination of the molecular mass of some liquids or solid substances that can be transferred into vapors without decomposition. In the figure bellow it is sketched an apparatus made by an evaporating tube A heated in a vapors bath B and communicating with a gradated test tube E, filled with water and turned in a vessel containing the same liquid.

The molecular mass determination by the Victor Meyer method.



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With the help of the device D it is let to fall into the tube A the vial C which has the measured quantity of substance. The temperature in B must be sufficiently high for the substance to be vaporized immediately. The substance gives an equal air volume υ that collects in the test tube E where it is measured. Is not necessary to know the vapor temperature from A because the air volume, read in the graduated test tube is equal to the volume that the substance would have if this would be vaporized in air at the temperature from the test tube E. It is sufficient to know the temperature of the air in the room, t, the pressure equal to the atmospheric pressure, p, from which is taken the pressure of the water column remained in E and the water vapors pressure at the temperature t.

From the known weight of the substance, the volume of vapors, the temperature and pressure, the mass of 22.4 L (in normal conditions) is made.

3. *Dumas Method* (1827)

Is for the determination of liquids molecular mass with not much high boiling points. It is used a thin glass balloon with narrowed neck (made in the flame) under the shape of a capillary tube. This balloon is weighted first with air then is weakly heated in the flame and is put with the capillary tube in the liquid in question so that, at cooling, to get a little in the tube. The balloon is sunk in a bath with the known temperature so mush as the capillary tube to surpass the bath level. The liquid from the balloon boils and the majority of vapors leave the balloon through the capillary tube interacting with the air from. When the liquid from the bath is completely vaporized, the tube is closed with a small flame and the balloon taken out of the bath is cooled, dried and weighted. The balloon volume is determined by knocking the tube and filling the balloon with water. It is so determined the vapor density, at the bath temperature in rapport with the air density at the room temperature and pressure.

For the known volume, weight of vapor, temperature, pressure, the weight of 22.4 L of vapor, at standard conditions is calculated.

Example: 140 mg of volatile liquid displace 40 c.c. of air; recalculated at standard conditions, what is molecular weight?

$$\frac{0.140\ \text{g}}{40\ \text{c.c.}} = \frac{x\ \text{g (M.W.)}}{22.400\ \text{c.c.}}$$

$$x\ (\text{M.W.}) = 78\ \text{g}$$

C.Solids (non–electrolytes)

The molecular weight of a non–volatile, non–ionized solute may be determined by its: depression of the freezing point
elevation of boiling point
lowering of the vapor pressure of the solvent.

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a.*Freezing Points and Boiling Points (of solutions)*:

It is used the following relation:

the freezing point of the pure solvent > the freezing point of the solution

Experimentally it was established that the decreasing of the freezing point of dilute solution is in direct relation with the concentration of the solute. The French chemist M. Raoult gave the law: "the molar decreasing of the freezing point of different soluts is the same for a given solvent."

The freezing point lowering in a dilute solution, when water is the solvent, is 1.86°C for one mole of non–ionized solute in 1.000 g of solvent. Many other solvents show different but consistent molar freezing point depressions.

Example: a sample of compound weighing 1.50 g is dissolved in 100 g of H_2O. The freezing point is lowered with 0.093°C. What is the approximate molecular weight of the compound?

1.50 g in 100 g of solvent are equivalent with 15.0 g in 1.000 g of solvent:

$$\frac{15.0}{0.093} = \frac{x\ (M.W.)}{1.86}$$

$$x\ (M.W.) = 300.$$

b.*Boiling Point Method*

The boiling point elevation in a solution when water is the solvent is 0.52°C for one mole of non–volatile, non–ionized solute in 1.000 g of solvent.

Many other solvents show different but consistent molar boiling point elevations.

Example: a sample of sugar weighing 17.1 g is dissolved in 100 g of water. The boiling point is raised with 0.26°C. What is the molecular weight of sugar?

17.1 g in 100 g of solvent are equivalent with 171.0 g in 1000 g of solvent

$$\frac{171}{0.26} = \frac{M.W.}{0.52}$$

$$M.W. = 342$$

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CHAPTER IV
ATOM

IV.1. FUNDAMENTAL PARTICLES

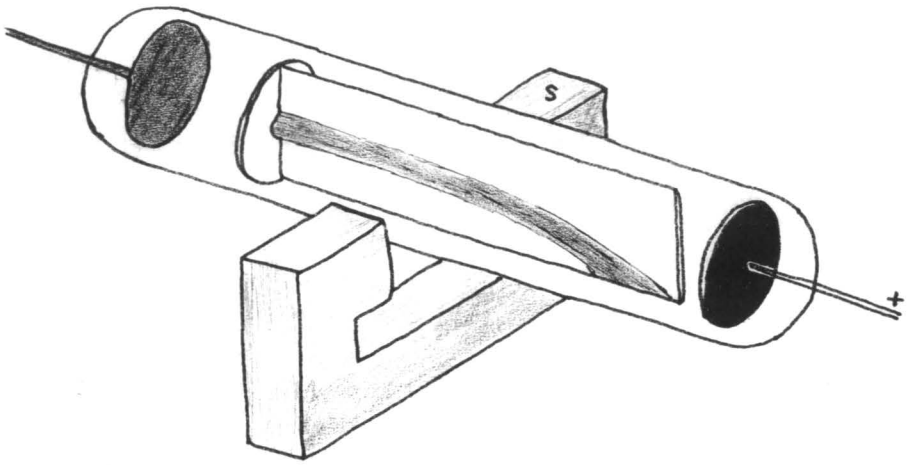
The notion that the matter consists of discrete particles in an old one. About 400 B.C. this idea appeared in the writings of Democritus, a Greek philosopher. He had been introduced to it by his teacher, Leucippus. The idea was rejected by Pluto and Aristotle, who had a great deal more influence in the development of ideas than Democritus. For nearly two thousand years, the concept of the atom remained just that, an abstract idea divorced from experimental reality.

The atomic and molecular theory gave us the notion that the atom is the smallest particle of the matter that cannot be broken down in other particles. The image was proved to be wrong by a series of discoveries in the XIXth century.

John Dalton, the father of atomic theory, said: "Thou can't split an atom". He was proven wrong by the combined efforts of J.J. Thomson (1856–1940), Ernest Rutherford (1871–1937) and James Chadwick (1891–1974), who discovered, in turn, the electron, the proton and the neutron.

In the 1890, J.J. Thomson studied the conduction of electricity through gases at low pressures. The apparatus used is illustrated in the figure bellow:

Cathode–ray tube. The ray is made up of fast–moving electrons. In an electric or magnetic field, the beam is deflected in such a way as to indicate that it carries a negative charge.



When the tube is partially evacuated and connected to a spark coil, an electric current flows through it. Associated with this flow are colored rays of light spreading out from the negative electrode (cathode). From the nature of the deflection of these cathode rays in an electric field, Thomson showed that they consists of a stream of negatively charged particle that he called electrons. He deduced that the electron is a tiny fraction of that of the atom.

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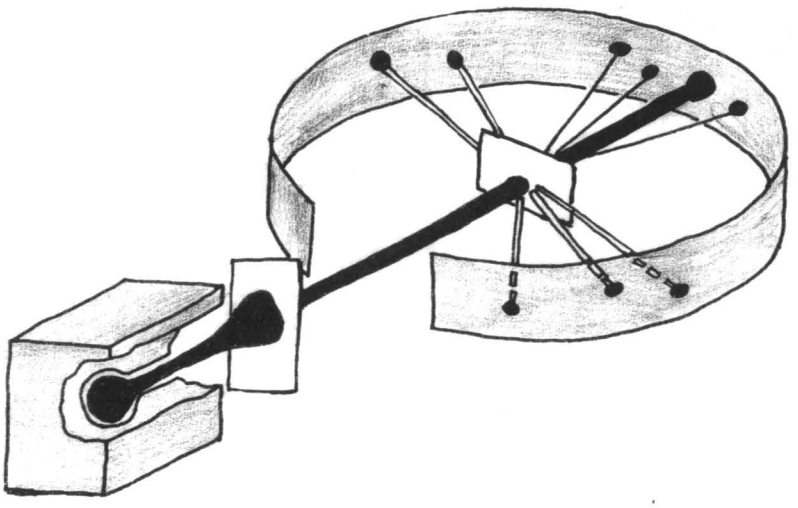
At the University of Manchester in England, Rutherfort directed a series of experiments that changed the idea about the structure of the atom. The experiments were carried out by Johannes Geiger and Ernest Marsden. They bombarded thin foils of gold and other metals with α–particles (He atoms minus their electrons). With a fluorescent screen, they observed the extent to which these particles were scattered. To no one's surprise, most of the α–particles passed through the foil unchanged in direction. A few, however, were reflected back at acute angles. This was a totally unexpected result, inconsistent with the model of the atom in vogue at that time. Eighteen months later, in 1911, Rutherford published an explanation. By a mathematical analysis of the forces involved, he showed that the atom must contain a tiny, positively charged nucleus according for most of its mass.

Rutherford scattering experiment. Most of the α–particles are essentially undeflected, but a few are scattered at large angles. In order to cause the large deflections, atoms must contain heavy, positively charged nuclei.

1)–lead shield; 2)–α–source; 3)–slit; 4)–gold foil; 5)–zinc sulfide screen;
6)–a few α particles are scattered at large angles;
7)–transmitted beam containing most of the α particles with only small deflection;



Once the existence of the nucleus had been established, scientists began to speculate upon its composition. In 1919, Rutherford announced the discovery of the proton. He showed that it was ejected from the nucleus of a nitrogen atom when it collides with an α–particle. A year later, Rutherford suggested that the nucleus must contain an uncharged particle with the same mass as the proton. In 1932 Chavendish discovered the neutron.

Some of the properties of these fundamental particles are listed in the table bellow.

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Properties of subatomic particles:

Particle	Location	Relative Charge	Relative Mass	Actual Charge (C = coulombs)	Actual Mass
Proton	nucleus	+1	1.0	$+1.6022 \times 10^{-19}$ C	1.6727×10^{-24} g
Neutron	nucleus	0	1.0	0	1.6750×10^{-24} g
Electron	outside nucleus	–1	0.00055	-1.6022×10^{-19} C	9.1095×10^{-28} g

It can be observed that protons and neutrons are located in the nucleus of an atom. The nucleus contains more than 99.9 % of the mass of the atom, even though its diameter is only about 1/10.000 of that of the atom.

The proton has a mass nearly equal to that of the lightest atom, the hydrogen atom. Reflecting that fact, the proton has an assigned mass number of 1. The proton carries a unit positive charge (+1). All atoms contain an integral number of protons in the nucleus; this number ranges from 1 to over 100. The neutron is an uncharged particle with a mass about equal to that of the proton. The neutron, like the proton, has a mass number of 1.

The electron carries a unit negative charge (–1), equal in magnitude but opposite in sing to that of the proton. The electron is much lighter than the proton or neutron; its mass is only about 1/2000 that of a hydrogen atom. In round number terms, we assign the electron a mass number of zero. The number of electrons in an atom, like the number of protons, can vary from 1 to over 100. The electrons are found in the outer regions of atoms, where they constitute what amounts to a cloud of negative charge about the nucleus.

Atomic Number

All the atoms of a particular element have the same number of protons in the nucleus. This number is a basic property of an element, called its atomic number:

atomic number = number of protons

In a neutral atom the number of protons in the nucleus is exactly equal to the number of electrons outside the nucleus. Consider, for example, the elements hydrogen (at. No. = 1) and helium (at. No. = 2). All hydrogen atoms have one proton in the nucleus; all helium atoms have two. In neutral hydrogen atom there is one electron outside the nucleus; in a helium atom there are two.

H atom:	1 proton,	1 electron,	atomic number = 1
He atom:	2 protons,	2 electrons,	atomic number = 2
U atom:	92 protons,	92 electrons,	atomic number = 92.

Atomic numbers of the elements are given in the periodic table and they increase steadily as we move across the table.

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Mass Numbers. Isotopes.

As with protons and neutrons, we can assign mass numbers to atoms. The mass number is found by adding up the number of protons and neutrons in the nucleus:

mass number = number of protons + number of neutrons

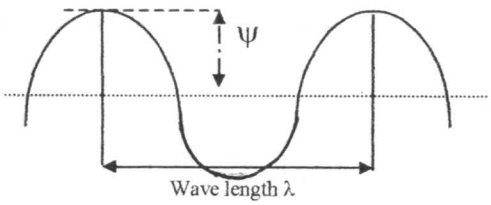
All atoms of a given element have the same atomic number (number of protons). They may, however, differ from one another in mass and hence in mass number. This can happen because, although the number of protons in the nucleus of a given kind of atom is fixed, the number of neutrons is not. It may vary and often does. Consider the element hydrogen (at. No. = 1). There are three different kinds of hydrogen atoms. They all have one proton in the nucleus. A "light" hydrogen atom (the most common type) has no neutrons in the nucleus (mass no. = 1). Another type of hydrogen atom (deuterium) has one neutron (mass no. = 2). Still a third type (tritium) has two neutrons (mass no. = 3).

Atoms that contain the same number of protons but a different number of neutrons are called isotopes. The three kinds of hydrogen atoms just described are isotopes of that element. They have masses that are very nearly in ratio 1 : 2 : 3. Quite often isotopes of an element are distinguished from one another simply by writing the mass number after the symbol of the element. For example, uranium has two isotopes: U–235 and U–238.

Isotope	Atomic Number	Mass Number	Number of Protons	Number of Neutrons
Uranium–235	92	235	92	143
Uranium–238	92	238	92	146

Quantum Theory

In 1873, Clerk Maxwell showed that the alternative moving (forward and back) of an electric charge exhibits the electromagnetic wave with the same properties as light. In 1888, Heinrich Hertz verified this experience and described the nature of the moving electromagnetic waves. For example, this wave resembles with the waves on the surface of the sea:



ψ – the amplitude (the height of the crust or the depth of a trough);

λ – wave length;

ν – frequency – the number of waves (successive crusts) that pass a given point

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in a second; $\nu = c / \lambda$

c – velocity at which a wave moves (the speed of light).

In 1900, Maxwell Planck explained the emission of light. Planck supposed that the absorption or emission of light with a given λ is only in a given part called quanta (a piece or a bit of energy) and this energy is proportional with the frequency:

$$E \sim \nu$$
$$E = h\,\nu; \quad \nu = 0.662 \cdot 10^{-33}\ J \cdot s.$$

In 1905, Albert Einstein called this portion of energy or light, quanta: photon with the energy

$$E = h\,\nu = h\,c/\lambda.$$

Today it is known the fact that the quantum theory is applied to all interactions of matter with energy.

– *basis of quantum theory*

Atoms can only exist in certain states, characterized by definite amount of energy. When an atom changes its state, it absorbs or emits an amount of energy equal with the difference between the energies of the states.

- the atomic energy arises from the motion of electrons around the nucleus.
- the atomic energy also arises from electrical interactions between electrons (carriers of negative charge) and the positively charged nucleus. This kind of energies is called electronic energy. The values of the electronic energy are not continuously (experiments of Planck and Einstein).
- these energies are organized in levels of energy. Each level correspond to certain energy and between them are not levels.
- the energy of systems that can exist only in discrete states is said to be quantified.
- the lowest electronic energy state is called the ground state. The states with energy greater then the one of the ground state are exited states.

Molecules and Ions

Isolated atoms rarely occur in nature. For the most part, they are too reactive to be found by themselves. Instead, atoms tend to combine with one another in various ways. As a result, the structural units in most elements and all compounds are more complex than simple atoms. Two of the most important "building blocks" of matter are molecules and ions, both of which are formed from atoms.

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Molecules

The basic structural unit in most volatile (easily vaporized) substance is the molecule. A molecule is a group of two or more atoms held together by strong forces called chemical bonds. Many elements consist of diatomic molecules. The hydrogen molecule is typical; its structure may be shown as:

H — H

where the dash is used to represent the bond joining the two hydrogen atoms. The molecule of the gaseous compound hydrogen chlorine is also diatomic. It has a structure:

H — Cl.

Most often, molecular substances are represented by molecular formulas:

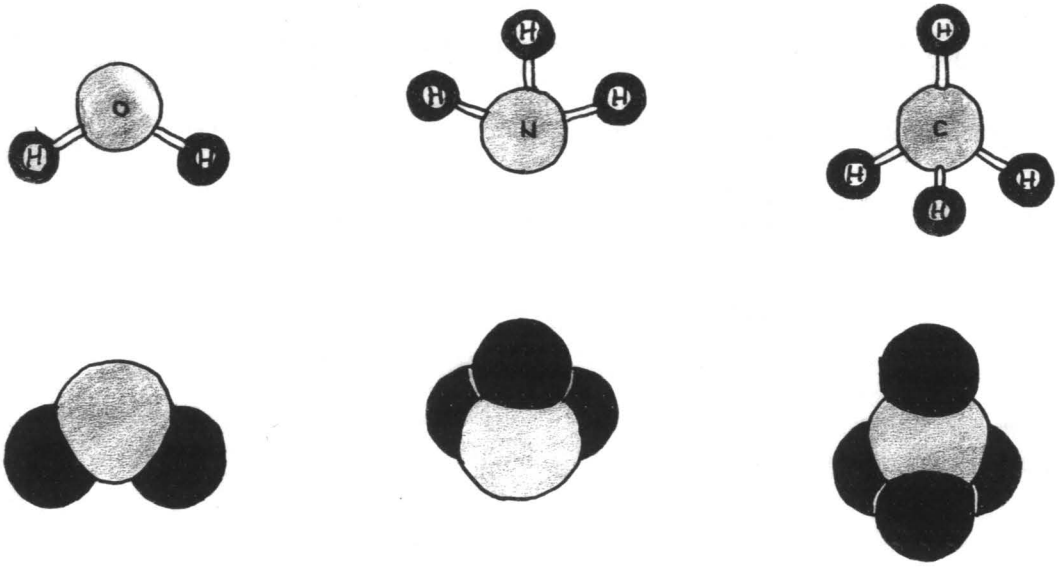
hydrogen: H_2 (2H atoms per molecule)

hydrogen chloride: HCl (1H atom, 1 Cl atom per molecule).

Most molecular substances are composed of molecules more complex than those just cited. The water molecule, H_2O, consists of a central oxygen atom bonded to two hydrogen atoms. In the ammonia molecule, NH_3, a central nitrogen atom is bonded to three hydrogen atoms. Methane, CH_4, the major component of natural gas, has as a structural unit a molecule in which a carbon atom is bonded to four hydrogen atoms.

Ball–and –stick and space–fill models of molecules H_2O, NH_3 and CH_4. In each case, the hydrogen atoms are bonded to a central, nonmetal atom (O, N, C).

Water (H_2O) Ammonia (NH_3) Methane (CH_4)



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Ions

If enough energy is applied, one or more electrons can be removed from a neutral atom. This leaves a positively charged particle somewhat smaller than the original atom. Electrons may also be added to certain atoms to form negatively charged particles larger than the original atom. Charged particles are called ions. An example of a positive ion (cation) is the Na^+ ion, formed from a sodium atom by the loss of a simple electron. Another cation is Ca^+, derived from a calcium atom by removing two electrons.

$$\underset{(11\,p^+,\,11\,e^-)}{\text{Na atom}} \rightarrow \underset{(11\,p^+,\,10\,e^-)}{Na^+\text{ ion}} + e^-$$

$$\underset{(20\,p^+,\,20\,e^-)}{\text{Ca atom}} \rightarrow \underset{(20\,p^+,\,18\,e^-)}{Ca^+\text{ ion}} + 2e^-$$

Two common negative ions (anions) are the chloride ion, Cl^- and oxide ion, O^{2-} These are formed when atoms of chloride or oxygen acquire electrons:

$$\underset{(17\,p^+,\,17\,e^-)}{\text{Cl atom}} + e^- \rightarrow \underset{(17\,p^+,\,18\,e^-)}{Cl^-\text{ ion}}$$

$$\underset{(8\,p^+,\,8\,e^-)}{\text{O atom}} + 2\,e^- \rightarrow \underset{(8\,p^+,\,10\,e^-)}{O^{2-}\text{ ion}}$$

When an ion is formed, the number of protons in the nucleus is unchanged. The number of electrons increases or decreases. Negative ions contain more electrons than protons; positive ions contain fewer electrons than protons. The charge of the ion is indicated by a subscript at the upper right. The O^{2-} ion has –2 charge; it has two more electrons than the oxygen atom. The Na^+ ion has a +1 charge; it has one fewer electron than the sodium atom.

Many compounds are made up of ions. They are called ionic compounds. Since a bulk sample of matter must be electrically neutral, ionic compounds always contain both cations (+ charge) and anions (– charge). Ordinary table salt, sodium chloride, is made up of an equal number of Na^+ and Cl^- ions, the same as for calcium oxide (quicklime): Ca^{2+} and O^{2-} ions.

The composition of an ionic compound is indicated by writing its formula. Here, subscripts are used to indicate the relative numbers of ions of each type.

Example:

Compound	Formula	Interpretation
Sodium chloride	NaCl	1 Na^+ ion for 1 Cl^- ion
Calcium oxide	CaO	1 Ca^+ ion for 1 O^{2-} ion
Sodium oxide	Na_2O	2 Na^+ ions for 1 O^{2-} ion
Calcium chloride	$CaCl_2$	1 Ca^{2+} ion for 2 Cl^- ions

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Avogadro's Number

Let's consider the elements helium and hydrogen. The helium atom is about four times as heavy as a hydrogen atom. From this it follows that a sample containing 100 helium atoms weights four times as much as 100 hydrogen atoms. The sample containing helium weighing four grams must contain the same number of atoms as a sample of hydrogen weighing one gram:

no. of He atoms in 4.003 g helium = no. of H atoms in 1.008 g hydrogen

This reasoning is readily extended to other elements. A sample of an element with a mass in grams equal to its atomic mass contains definite number of atoms, N, regardless of the identity of the element. Several ingenious experiments have been designed to determine this number N, known as Avogadro's name. It resulted that the Avogadro's number is:

$$6.022 \times 10^{23}.$$

The importance of Avogadro's number in chemistry should be clear. *It represents the number of atoms in a sample of an element with a mass in grams numerically equal to its atomic mass.* Thus there are:

6.022×10^{23} H atoms in 1.008 g H	atomic mass H = 1.008 a.m.u.
6.022×10^{23} He atoms in 4.003 g He	atomic mass He = 4.003 a.m.u.
6.022×10^{23} S atoms in 32.07 g S	atomic mass S = 32.07 a.m.u.

Knowing Avogadro's number and the atomic mass of an element, it is possible to calculate the mass of an individual atom or the number of atoms in the sample.

Mole

Since atoms and molecules are so small, it is convenient to talk about groups of 6.022×10^{23} of them. This counting unit has a special name: the mole (abbreviated as mol). So, a mole means Avogadro's number of items. Thus:

1 mol H atoms = 6.022×10^{23} H atoms
1 mol O atoms = 6.022×10^{23} O atoms
1 mol H_2 molecules = 6.022×10^{23} H_2 molecules
1 mol H_2O molecules = 6.022×10^{23} H_2O molecules
1 mol electrons = 6.022×10^{23} electrons

This definition allows the direct conversion between moles and numbers of particles. For example,

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$$\text{no. particles in } 1.24 \text{ mol} = 1.24 \text{ mol} \times \frac{6.022 \times 10^{23} \text{ particles}}{1 \text{ mol}}$$

$$= 7.47 \times 10^{23} \text{ particles}$$

$$\text{no. particles in } 3.24 \times 10^{22} \text{ particles} = 3.24 \times 10^{22} \text{ particles} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ particles}}$$

$$= 0.0538 \text{ mol.}$$

In general, one mole of atoms of any element has a mass in grams numerically equal to the atomic mass of the element. This idea can be extended to substances that consist of molecules or ions. For substances represented by the formulas H_2, H_2O and NaCl:

1 mol H_2 cotains 2 mol H atoms and weighs 2(1.01 g) = 2.02 g
1 mol H_2O contains 2 mol H atoms and 1 mol O atoms and weighs
2(1.01 g) + 16.00 g = 18.02 g
1 mol NaCl contains 1 mol Na atoms (22.99 g) and 1 mol Cl atoms
(35.45 g) and weighs 22.99 g + 35.45 g = 58.44 g

In general, it can be said that, for any substance, the mass of one mole in grams is given by the formula mass, defined to be the sum of the atomic masses in the formula.

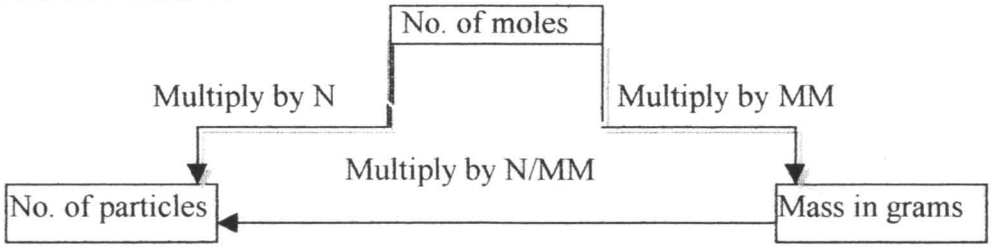
Formula	Formula Mass	Molar Mass
He	4.003 a.m.u.	4.003 g/mol
H_2	2(1.008 a.m.u.) = 2.016 a.m.u.	2.016 g/mol
H_2O	2(1.008 a.m.u.) + 16.00 a.m.u. = 18.02 a.m.u.	18.02 g/mol
NaCl	22.99 a.m.u. + 35.45 a.m.u. = 58.44 a.m.u.	58.44 g/mol

In other words, the molar mass of a substance, in grams per mole, is numerically equal to its formula mass.

The formula mass of a substance can be found by simply adding the atomic masses of the atoms in the formula. If the formula consists of a single atom, as with helium, the formula mass is the atomic mass. If the formula corresponds to a molecule like H_2 or H_2O, the formula mass is the molecular mass (the molecular mass of H_2 is 2.016 a.m.u.).

In order to find the molar mass of a substance, we must know its formula.

Mole – gram conversions:



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Conversion between numbers of particles, numbers of moles and masses in grams can be made using:

N = Avogadro's number = 6.022×10^{23} particles/mole

MM = molar mass (g/mol)

Molarity (M): represents the number of moles of solute per liter of solution. Specially, molarity is defined by the equation:

$$\text{Molarty} = \frac{\text{number moles solute}}{\text{number liters solution}}$$

A solution containing 1.20 g mol of solute in 2.50 L of solution would have a molarity of: 1.20 mol / 2.50 L = 0.48 mol/L

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IV.2. **Development of the atomic theory**

One of the oldest scientific concepts is that all matter can be broken down until finally the smallest possible particles are reached, particles that cannot be subdivided further.

Dalton's atomic theory

The development of the atomic theory involved contributions from many individuals, but there was one man whom we associate particularly with the origin of modern atomic theory. He introduced the name atom as a invisible particle. Dalton's atomic theory was developed during the period 1803–1808 and was based on three principal assumptions.

(a) Each chemical element is composed of minute indivisible, indestructible particles called atoms. Atoms can be neither created nor destroyed during a chemical change.
(b) All atoms of a given element are alike in mass and properties.
(c) In chemical compounds, atoms of different elements are united in simple numerical ratios (AB) or (AB_2).

Experiments

1. Cathode rays

The more significant properties of cathode rays determined by Plucker, Hittorf, Grookes are:

1. Cathode rays are emitted from the cathode in an evacuated tube when electric current is passed.
2. The rays travel in straight lines.
3. The rays, upon striking glass or certain other materials, cause them to fluoresce (give off light). Only in this way can they be seen; the rays themselves are invisible.
4. Cathode rays are deflected by electric and magnetic fields in the manner expected for negatively charged particles.
5. The properties of cathode rays are independent of the electrode material.

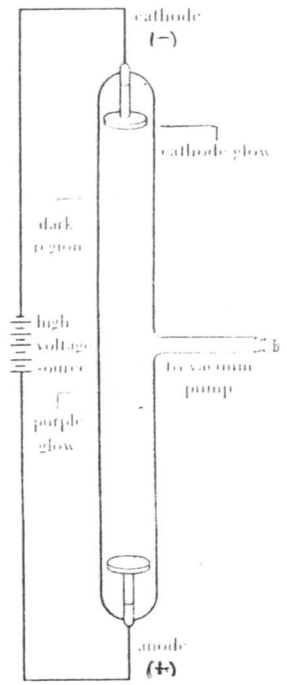

Fig.II.1.–Electric discharge in an evacuated chamber.

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2. **Charge of electron**

J.J. Thomson's investigations proved a precise ratio of charge to mass for an electron.

The cathode rays are deflected by an electric field **E** and by a magnetic field **H**.

The magnetic force $\rightarrow$ Hev

The electric force $\rightarrow$ Ee

$$Hev = mv^2/r; \quad Hev = Ee; \quad v = E/H$$
$$e/m = v/Hr; \quad e/m = E/H^2r$$
$$e/m = 1.759 \cdot 10^8 \text{ C/g}$$

e/m is independent from the nature of the cathode and the gas of the tube.

2.2.3. Canal Rays (Positive Rays)

In 1886, Eugene Goldstein performed a series of experiments in which he discovered a new type of particles called canal rays or positive rays. Some of the properties observed for these rays are the following:

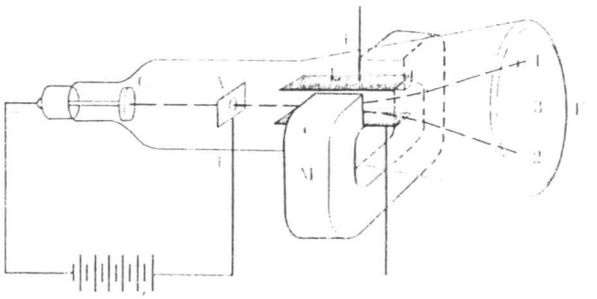

Fig. II.2.–Thomson's apparatus for determining the charge to mass ratio, e/m, for cathode rays.

Code: C: cathode; A: anode (perforated to allow the passage of a narrow beam of cathode rays); E: electrically charged condenser plates; M: magnet; F: fluorescent screen.

1. The particles are deflected by electric and magnetic fields in a way that reveals their positive charge.
2. The ratio of charge to mass e/m, for positive rays is considerably for smaller than for electrons.
3. The e/m ratio depends of the gas in the tube.

3. **X–Rays**

A number of cathode ray experimenters, including apparently J.J. Thomson himself, occasionally observed objects outside the cathode ray tubes to glow when the tubes were run. It remained for W. Roentgen to show that the impact of cathode rays (electrons) on a surface produces a type of radiation, which, in its turn, can cause

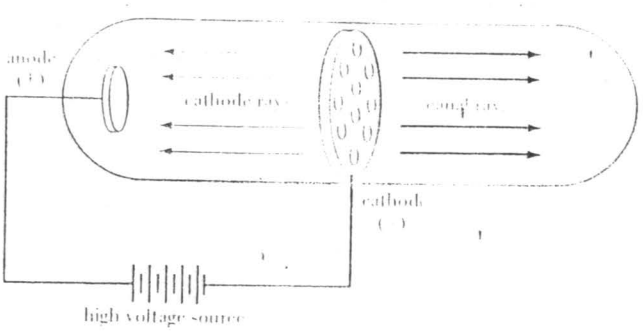

Fig. II.3–A canal ray tube

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certain substances to glow at a distance from the cathode ray tube. Because of the unknown nature of this radiation, the term X ray was coined, a name still in common use.

4. **Radioactivity**

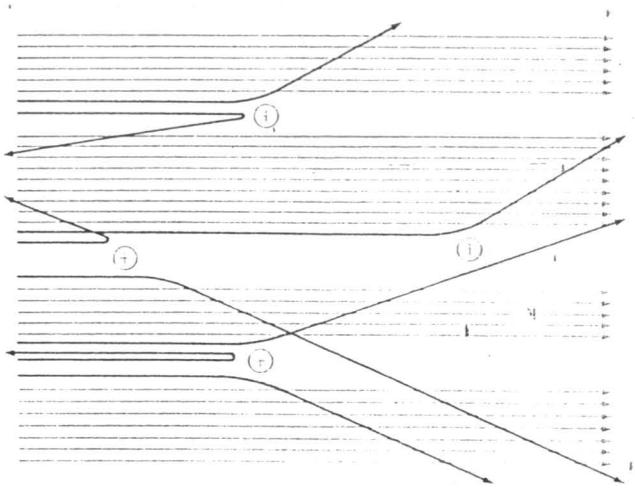
E. Rutherford was able to show that two types of radiation existed. One type, which Rutherford called alpha rays **α**, has a high ionizing power but a low penetration through matter. Alpha rays can be stopped by a sheet of ordinary paper. The other type is of a lower ionizing power but greater penetrating power. These rays can pass through aluminum foil up to 3 mm thick. Rutherford called this radiation beta rays **β**.

Alpha rays are particles carrying two fundamental units of positive charge and have a mass equal to that of helium atom; thus a particle is identical to the ion He^{2+}.

Beta rays are negatively charged particles with the same charge–to–mass ratio, e/m, as electron. A third form of radiation has an extremely high penetrating power and is deflected by electric and magnetic fields. This electromagnetic radiation is known as gamma rays **γ**.

Scattering of **α** particles – Figure II.4.

Figure II.4–Rutherford's interpretation of the scattering of α particles by metal foil.
Each arrow represents a α particle.
The symbol represents an atomic nucleus.



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Rutherford's atomic model

The main feature of the atom postulated by Rutherford were these:

1. Most of the mass and all of the positive charge of an atom are centered in a very small region called the nucleus.
2. In the atom there is empty space.
3. There must be a number of electrons outside the nucleus of an atom that is equal to the number of units of nuclear charge (to account for the fact that the atom is electrically neutral).

Electrons in Atoms

A knowledge of atomic structure helps us to understand the forces between atoms that lead to the formation of molecules. To understand the behavior of electrons in atoms requires some appreciation of the nature of electromagnetic radiation. Our study will begin with this topic. We will see how experiments and discoveries followed one another, for the most part in a logical fashion.

1. Electromagnetic Radiation

The mode of propagation of the electric or magnetic field is called a **wave**. The product of the length of the wave λ and the number of cycles produced per second υ indicates how the wave front has traveled down the string in **1s**. This is the velocity of wave, **c**.

2. Atomic Spectra

Among the most extensively studied atomic spectra during the nineteenth century was that of the element hydrogen.

In 1855, the Swiss physicist–school teacher J. Balmer deduced the following formula for λ:

$$\lambda\,(\text{in Å}) = 3645.6 \times \frac{n^2}{n^2 - 4}$$

where n = 2, 4, 5.

A more commonly encountered form of the Balmer equation is shown below, written in terms of the frequencies of the spectral lines.

$$\upsilon_n = Rc \times \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$$

where: R = Rydberg constant ($10.967.800\ m^{-1}$)

c = velocity of light

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3. **Quantum Theory**

In 1900 Max Planck explained a phenomenon known as blackbody radiation. Planck's revolutionary hypothesis was that the energy (like matter) is discontinuous and consists of large numbers of tiny discrete units called ***quanta***.

The energy associated with a quantum of electromagnetic radiation is proportional to the frequency of the radiation and is expressed by

$$E = h\upsilon$$

where: υ = the frequency of light

h = Planck's constant (6.6252×10^{-27} erg $\times$ sec).

4. **Bohr's Theory of Atoms**

The culmination of the development of the concept of quantization, prior to advent of wave mechanics, was Bohr's theory of the hydrogen atom.

In 1913, a Danish physicist, Niels Bohr produced a solution to this dilemma through an interesting combination of classical and quantum theory. His description of the hydrogen atom depicted the electron as orbiting around the nucleus, much as the earth revolves about the sun. It has been called the solar system atomic model. The basic assumptions of Bohr's theory were these:

1. There is a certain set of allowable orbits for an electron in a hydrogen atom. These orbitals referred to as stationary states of motion, are circular paths around the nucleus. The motion of an electron within a stationary state can be described by ordinary mechanics. However even though classical theory would predict otherwise, as long as an electron remains in a stationary state its energy remains constant and it does not emit light.

On the stationary state: from classical physics the centrifugal force may be equated with the coulombic attraction

$$-q_1q_2 / r^2 = mv^2 / r$$

$$Ze^2 / r^2 = mv^2 / r$$

$$Ze^2 = mv^2r \qquad \text{(classic mechanic)}$$

2. The allowable stationary states are those in which certain properties of the electron have unique values. In particular, a property called the angular momentum must be an integral multiple of $h/2\pi$, that is, the angular momentum must be $n\ h/2\pi$ (where n is an integer number and h is Planck's constant).

$$mvr = n\ h/2\pi$$

3. An electron can pass only one stationary state to another. In such transitions fixed, discrete amounts of energy (quank) are involved.

$$E_2 - E_1 = \Delta E = h\upsilon$$

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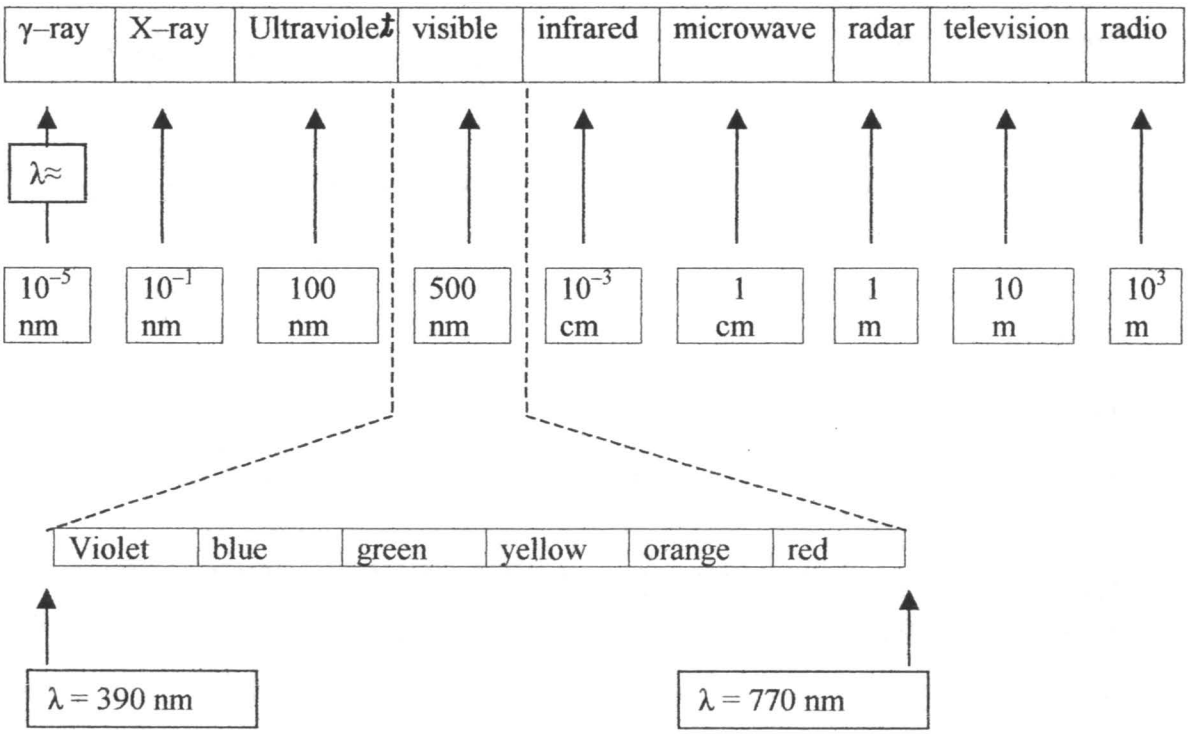
Fig. II.5. The Electromagnetic Spectrum



The total energy, E, is the sum of kinetic and potential energy:

$$E = 1/2\ mv^2 - Ze^2/r$$

and

$$E = -1/2\ Ze^2/r$$

From these equations:

$$v = Ze^2\ 2\pi/nh$$

$$r = \frac{n^2\ h^2}{4\ \pi^2\ m\ Ze^2}$$

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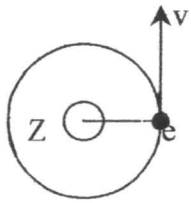
$$E = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2} = -\frac{R}{n^2}$$

Bohr model of hydrogenlike atoms:



Bohr derived equations for the radius and energy, respectively, of the electron in its various orbits about the nucleus.

$$r = \frac{n^2 h^2}{Z\, 4\pi^2 \mu e^2} = n^2 \frac{a_o}{Z} \qquad (1\text{–}2)$$

$$E = -Z^2 \frac{2\pi^2 \mu e^4}{n^2 h^2} = -\frac{R}{n^2} \qquad (1\text{–}3)$$

Z – is the charge on the nucleus in atomic units
h – Planck's constant
e – the charge of the electron
μ – the reduced mass of the electron
n – quantum number
a_o – the radius of the most stable orbit (n=1) of the hydrogen atom; the Bohr radius
R – Rydberg constant

Bohr's theory was in remarkable agreement with many experimental facts and proved the first satisfactory explanation of the line spectra of atoms (fig. III.1)

For example, one can compute easily from equation (1–3) the energy required to ionize the atom in its ground state, that is to separate the electron and proton to an infinite separation with each at rest. We indicated on the diagram the values of the energies.

In figure III.1. the energies associated with the different allowable states for the electron in a hydrogen atom are shown as a group of lines. Electron transitions from higher quantum number levels to the level n=1 produce lines in the Lyman series; n=2 the Balmer series; n=3 Brakett series; n=4 …

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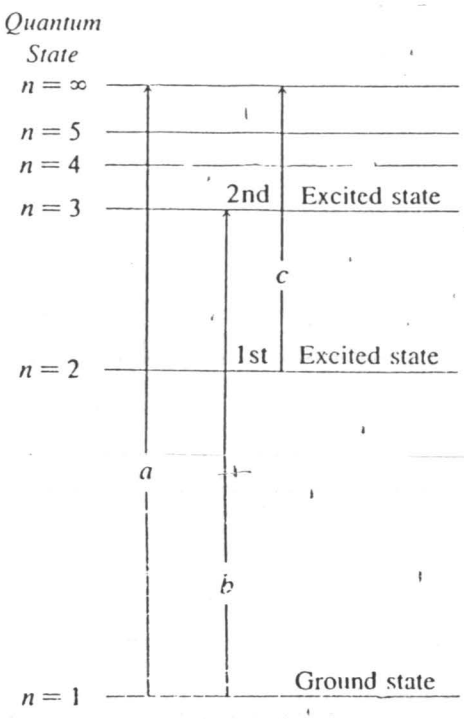

Figure III.1.

Energy – level diagram for the hydrogen atom

For atomic H the terms take the form R / n^2 where R is a constant called the Rydberg constant (having a value of 109.677589 cm^{-1}).

Thus empirically, all lines of the spectrum of atomic hydrogen have wave numbers given by the equation:

$$1/\lambda = \omega = R/n_1^2 - R/n_2^2 = T_1 - T_2$$

where $1/\lambda$ is the wave number.

According to Bohr's theory, $h\upsilon = E_1 - E_2 = hc\omega$.

From Bohr's theory, the Rydberg constant is given by $2\pi^2 me^4 / h^3 c$.

The excellent agreement between the value calculated from these fundamental constants and the spectrocopically derived value gave strong support to Bohr's theory.

The Bohr's theory, with some modifications, was found to be capable of explaining the Moseley relationship between characteristic X–ray spectra and atomic number. The excited state for emission of X–ray was postulated as one in which a low–energy electron had been knocked out of a polyelectron atom. An electron from a higher energy state could then drop down to the lower empty orbit. In a polyelectron atom a given electron will be shielded partially from the positive charge may be taken as $Z - \sigma$ where σ represents the shielding effect of underlying electrons. For an electron dropping from n = 2 state to n = 1 state in a polyelectron ion, the Bohr theory thus would predict:

$$\upsilon = \frac{2\pi^2 m(Z-\sigma)^2 e^4}{h^3}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

or

$$\upsilon = 3/4\ Rc(Z-\sigma)^2$$

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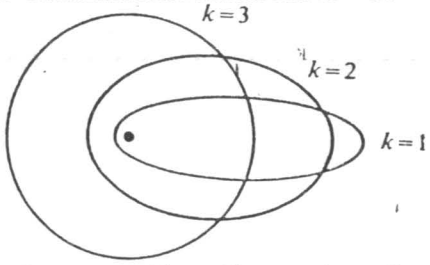
5. **Bohr–Sommerfeld Model of the Atom**

Sommerfeld modified the Bohr treatment by specifying that electrons travel in elliptical orbits, with the nucleus at one of the foci–circular orbits being simply a special case of elliptical orbits. The electron travel in an elliptical orbit would have, in addition to its angular momentum, a component of momentum along the radial direction. Both moments were quantified: that is, taken as units of $h/2\pi$. The two resulting quantum numbers were called azimuthal quantum number, designated as k and the radial quantum number n_r.

The sum of these quantum numbers, $k + n_r$, corresponded to the principal quantum number of n of the Bohr theory. The possible orbits for $n = 3$ are shown in figure III.2.

Figure III.2. Bohr–Sommerfeld orbits for n = 3.



The quantum numbers n and k suffice to describe elliptical orbits in a plane, but another quantum number is necessary to describe the orientation of the plane of the ellipse in space.

Not all orientations are possible – only those in which the component of momentum along the z axis is quantified. Since the energies of the states corresponding to different orientations differ in a directional magnetic field, the quantum number associated with these states is called the magnetic quantum umber (m_e).

Finally, Goudsmit and Uhlenbeck postulated that the electron itself has a spin and a corresponding spin angular momentum, which is quantified, only a spin angular quantum momentum of $1/2(h/2\pi)$ being allowed.

In a directional magnetic field the momentum associated with the spin can only be parallel or antiparallel to a magnetic field, thus giving rise to a magnetic spin quantum number, $m_s(s)$.

6. **The Beginning of Wave Mechanics**

According to wave mechanics, any system (an atom, a molecule) is described by a state function or wave function, symbolized by ψ, which is a function of the coordinates of all the particles constituting the system.

In order to understand why ψ is called a wave function and why wave mechanics presupposes that we cannot precisely define the position of an electron, we may consider some developments in physics which occurred just prior to the formulation of wave mechanics by the physicist Erwin Schrödinger.

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De Broglie proposed that we could associate with a beam of electrons a wavelenght, λ, given by:

$$\lambda = h / p,$$
$$p = mv$$
$$\lambda = h/mv = h/mc.$$

h = the Planck constant

p = the momentum of an electron in the beam.

The physical reality of this wave nature of the electron was demonstrated in 1927 by Davisson and Germer and by Thomson who shown that a beam of electrons could be diffracted by a suitable greeting in a manner analogous to the diffraction of a beam of light.

7. **The Wave Equation**

The form of the wave equation, which applies to a stationary state of a system, can be written in an exceedingly simple symbolic form:

$$H\psi = E\psi$$

H – represents a certain way of expressing the total energy of the system

E – is the numerical value of that energy.

For all system which will normally concern us as chemists, the total energy is just the sum of the kinetic energy, T, and the potential energy, V, that is: $H = T + V$.

H – is frequently called the Hamiltonian of a system

We consider the Bohr model of the hydrogen atom with the fixed nucleus and the electron goes around it.

The kinetic energy T is given by: $T = 1/2mv^2$.

m – the mass of the electron

v – is the velocity.

The potential energy of the system: $V = -e^2/r$.

e – electronic charge

r – is the radius of the orbit.

$$H = 1/2\ mv^2 - e^2/r$$

or

$$H = p^2/2m - e^2/r \qquad p = mv.$$

In the Hamiltonian the classical momentum p is replaced with a derivative form:

$$p \rightarrow i \frac{h}{2\pi} \left(\frac{\delta}{\delta x} + \frac{\delta}{\delta y} + \frac{\delta}{\delta z} \right)$$

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$$H = -\frac{h^2}{8\pi^2 m}\left(\frac{\delta}{\delta x} + \frac{\delta}{\delta y} + \frac{\delta}{\delta z}\right) - \frac{e^2}{r}$$

$$\left(-\frac{h^2}{8\pi^2 m}\left(\frac{\delta}{\delta x} + \frac{\delta}{\delta y} + \frac{\delta}{\delta z}\right) - \frac{e^2}{r}\right)\varphi = E\varphi$$

This is the wave equation for the hydrogen atom.

8. **The Meaning of the Wave Equation**

In fact $\psi(x, y, z)$ has a particular value for any particular combinations of values of x, y, z. The physical meaning of this value is that it is related to the probability that the electron will be found at that point. The probability, P, of finding the electron at the point (x, y, z) is given by $P = \psi(x, y, z)\, \psi^*(x, y, z)$.

ψ^*: is the complex conjugate of ψ; since ψ can have imaginary values, we must in general multiply it by its complex conjugate in order that P be real. If ψ is real, $\psi^* = \psi$. The ψ function must satisfy the following requirements:

1. It must have value at each and every point.
2. It must not have the value ∞ at any point.
3. Its absolute value at all points must be such that.

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \varphi(xyz) \cdot \varphi^*(xyz)\, dx\, dy\, dz = \int \varphi\, \varphi^*\, d\tau = 1$$

The left term in equation gives us the sum of the probabilities of finding the electron at each point throughout all space. When a wave function satisfies this condition it is said to be normalized.

9. **The Hydrogen Atom**

The transformation into polar coordinates of the wave equation for the hydrogen atom:

$$\frac{d^2\varphi}{dx^2} + \frac{d^2\varphi}{dy^2} + \frac{d^2\varphi}{dz^2} + \frac{8\pi^2 m}{h^2}(E - V)\varphi = 0.$$

facilitates the separation of variables and solution of the equation. The position variables in polar coordinates are r = the radial distance of a point from the origin, θ = the inclination of the radial line to z axis, ϕ = the angle made with the x axis by the projection of the radial line in the xy plane (figure III.3)

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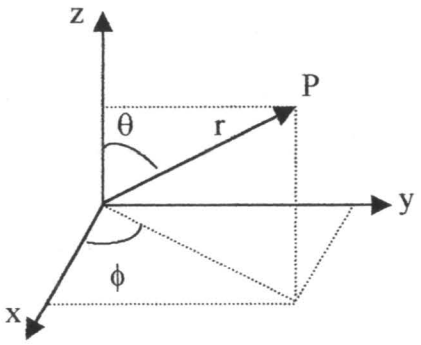
Figure III.3. Variables of polar coordinates.



$\varphi(x, y, z) \rightarrow \varphi(r, \theta, \phi)$

$\varphi(r, \theta, \phi) = R(r) \cdot \theta(\theta) \cdot \phi(\phi)$.

$\psi(r, \theta, \phi)$ is the solution of the wave equations:

$$\frac{1}{r} \cdot \frac{d}{dr} r^2 \frac{d}{dr}$$

If we substitute this expression with R(r), $\theta(\theta)$, $\phi(\phi)$ we get:

–the LHS of equation depends only on r whereas the RHS depends only on θ and ϕ.

–for R(r) the lowest energy correspond to a function ψ_1 which has the following rather simple form:

$$\psi_1 = \frac{\text{Exp}\left(-\frac{r}{a_o}\right)}{\sqrt{\pi}\, a_o^{3/2}}$$

a_o: the Bohr radius

r: the distance from the nucleus. It should be recognized that these functions are spherically symetrical, since their values do not depend on the angles θ and ϕ.

Another way, we consider the space around the nucleus to be divided into an infinite number of infinitesimally thin concentric spherical shells and ask what is the probability that the electron will be found in each of these. The total volume of such a shell of thickness Δr, is $4\pi^2 r^2 \Delta r$ and the total probability of finding the electron within it is $(4\pi^2 r^2 \Delta r)\psi_1^2$. In figure III.5. we ploted $4\pi^2 r^2 \psi_1^2$ against r. The maximum lies at a value of Δr equal to a_o.

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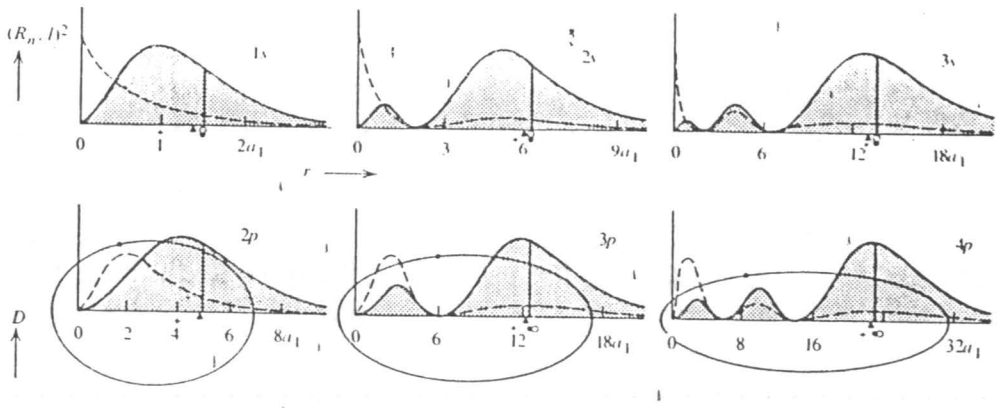
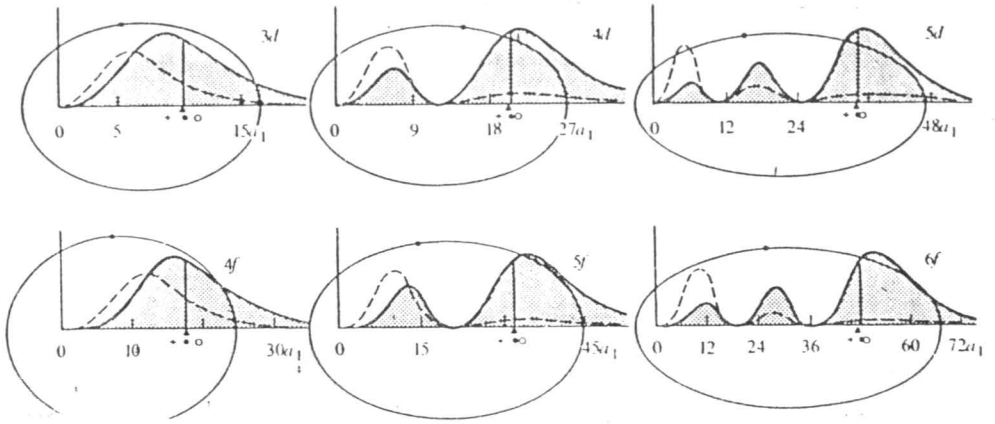
In figure III.4. is a plot of ψ_1 and ψ_1^2.

Figure III.4. Plot of ground state function ψ_1 and ψ_1^2 for hydrogen atom.



Thus although Bohr's model of the hydrogen atom led to the conclusion that in the ground state the electron would always be found going around the proton on a circular path exactly a_o in radius, wave mechanics says only that this is the most probable radius.

Figure III.5. Probability density function, $4\pi r^2 \psi_1^2$ or the ground state orbital of the hydrogen atom.



10. **The Hydrogen Atom Orbitals**

The three quantum numbers n, l and m, which arise in the solution of the wave equation, may each be considered to have a physical meaning. n gives a measure of the energy of an electron in an orbital:

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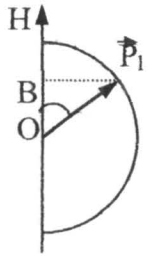
$$E_n = -\frac{1}{n^2}\frac{2\pi^2 m^2 e^4}{h^2}$$

The energy between the states with n = 1 and n = ∞ is the ionization energy of the atom. The quantum number n is also a measure of the mean radial distance of the electron density from the nucleus as shown in figure III.6.

l – the quantum number l can be taken as the measure of the classical angular momentum of the electron, although in wave mechanics this concept is not physically defined because we no longer visualize the electron as a discrete body with a definite position and velocity. The magnitude of the orbital angular momentum is given by $\sqrt{l(l+1)}\ h/2\pi$ is often taken as the unit of angular momentum. For example s electrons have angular momentum zero; p electrons (l = 1) have $\sqrt{1(1+1)} = \sqrt{2}$ units and d electrons (l = 2) have $\sqrt{6}$ units.

m – tells how the orbital angular momentum is orientated relative to some fixed direction, the magnetic field H.



The projection of the orbital angular momentum p_l on the H direction is quantified by m:

$$\overline{OB} = mh \qquad p_l = lh$$

$$\cos\alpha = OB/p \qquad p_l \cos\alpha = \overline{OB}$$

$$l\cos\alpha = m$$

For α = 0: cos α = +1, 0, –1 and m = –1, 0 1.

The quantum number (m) m = (2l + 1) values. Actually, the angular momentum vector should be regarded as processing about the reference direction, tracing out a cone of light m_e, as shown in figure III.6. for a p orbital.

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Figure III.6.

a) Plots of radial wave function R against r/a_o
b) Plots of density distribution functions $4\pi r^2 \psi^2$, against r/a_o ordinates only relative.

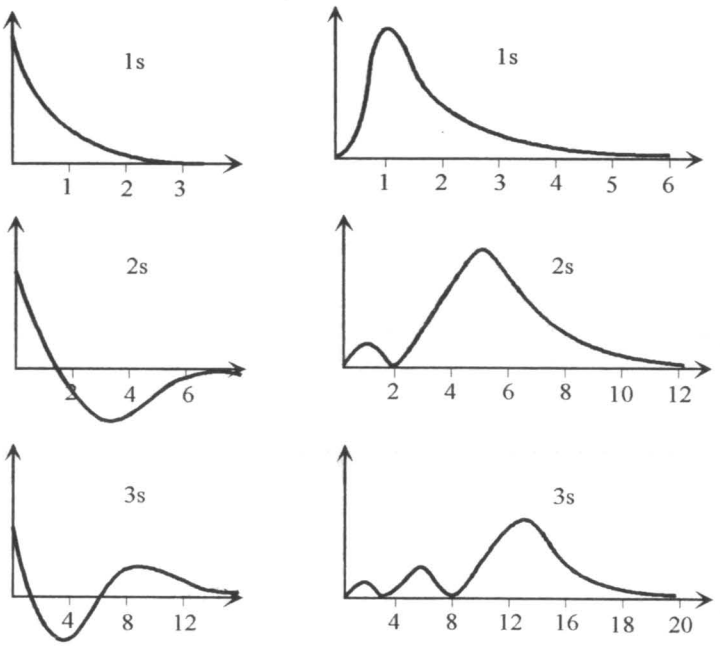
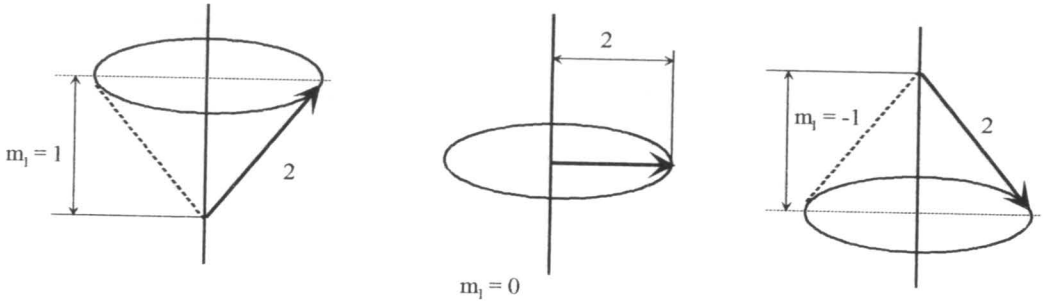


Figure III.7. **a** **b**

The three projections of the angular momentum vector of length $\sqrt{l(l+1)} = \sqrt{1(1+1)} = \sqrt{2}$, for a p orbital to give m_l values.



Orbitals:

s orbitals – there is an s orbital in every principal shell, that is, in every group of orbitals with the same principal quantum number.

It may be inferred from table 1 that all s orbitals are spherically symmetrical since they have an angular wave function which is independent of the angles θ and ϕ.

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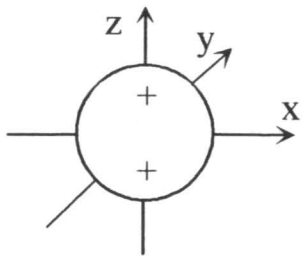
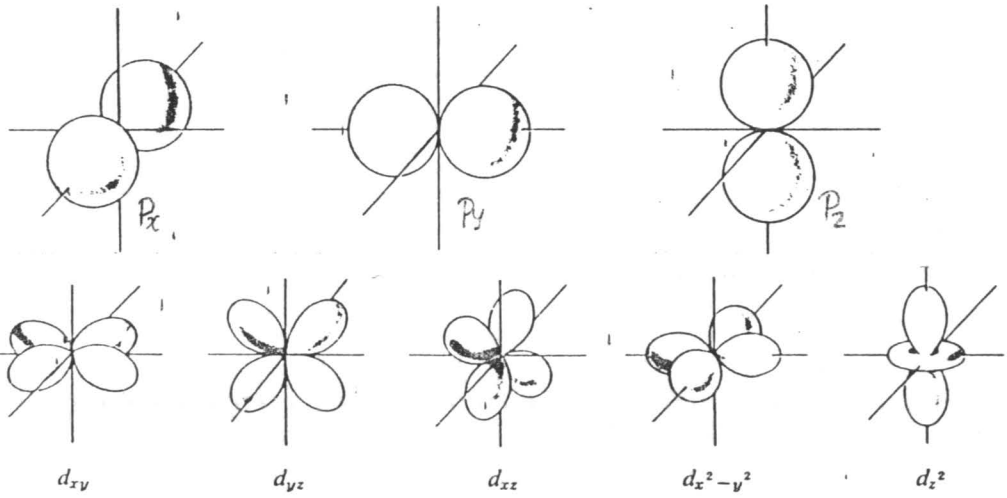


p orbitals – beginning with n = 2, each principal shell has three p orbitals. From table 1 we see that depend upon the angles θ and ϕ and thus are not shperically symmetrical. The three p orbitals in each set are classified as p_x, p_y and p_z.



d orbitals – beginning with n = 3 each principal shell will have a set of five d orbitals. They have the same radical dependence, but differ considerably in their angular distribution.

Table III.1.

HYDROGEN ATOM PROPERTIES FROM BOHR MODEL

Property	Formula*	Value for $n = 1$
r (radius)	$n^2\left(\frac{\hbar^2}{me^2}\right)$	0.529 Å $= a_0$
v (velocity)	$\frac{1}{n}(e^2/\hbar)$	2.19×10^8 cm sec^{-1} $= v_0$
t (period)	$n^3\left(\frac{2\pi\hbar^3}{me^4}\right)$	1.52×10^{-16} sec $= \tau_0$
E (energy)	$-\frac{1}{n^2}\left(\frac{e^4m}{2\hbar^2}\right) = -\frac{1}{n^2}\left(\frac{e^2}{2a_0}\right)$	-13.6 eV $= E_0$
μ (magnetic moment)	$\frac{evr}{2} = n\left(\frac{e\hbar}{2m}\right)$	0.927×10^{-20} erg/gauss $= \beta_e$
H (magnetic field at nucleus)	$\frac{e/t}{2r} = \frac{1}{n^5}\left(\frac{m^2e^7}{4\pi^2\hbar^5}\right)$	1.25×10^5 oersted

*$\hbar = h/2\pi = 1.055 \times 10^{-27}$ erg sec
$m = 9.109 \times 10^{-28}$ gm
$e = 4.803 \times 10^{-10}$ e.s.u.
n = orbital quantum number
a_0 is called the "Bohr radius"; β_e is called the "Bohr magneton".

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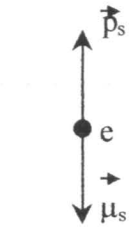
11. **Electron Spin**

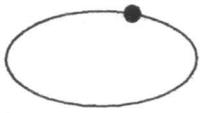
The electron possesses an inherent momentum called spin. The magnitude of the angular momentum in units $h/2\pi$ is given by the expression $\sqrt{s(s+1)}$ where the spin quantum number s takes the value 1/2, with the components +1/2 and –1/2 with respect to a reference direction. By analogy to m_l, we define the quantum number m_s and say that its values are limited to $\pm 1/2$.

The spin of the electron, which corresponds to the classical concept of rotation of the spherical electron about an axis through its center, causes it to have an inherent magnetic moment (μ_s) with the same magnitude and in the contrary sense as the spin kinetic momentum (p_s).



$$p_s = sh/2\pi$$

The projection of p_s with respect to a reference direction of the magnetic field (H) is quantified by m_s which takes 2s + 1 values (–s, 0, +s). In its mo–tion on the circular or elliptical orbit, the electron produces an electric current:



i = the intensity of the electrical currnet
S = the surface withi the orbit.

The dipol momentum

$$\mu_l = i \cdot S \cdot \varepsilon_o$$

$$S = \pi \cdot r^2 \qquad i = e \cdot V \qquad V = v/2\pi r$$

$$\Rightarrow i = e \cdot v/2\pi r \Rightarrow \mu_l = e \frac{v}{2\pi r} \cdot \pi \cdot r^2 \cdot \varepsilon_o = e \frac{m v r}{2m} \cdot \varepsilon_o = \frac{\varepsilon_o \cdot e}{2m} \cdot p_l$$

$$\mu_l = l \cdot \frac{\varepsilon_o \cdot e}{2m} \cdot \hbar$$

e/2m : the giromagnetic factor

$\frac{e\varepsilon}{2m}$ h : the magnetism quanta μ_B (Bohr magneton)

By analogy with μ_l :

$$\mu_S = e/2m \cdot p_s$$

the magnitude of: $p_s = \sqrt{s(s+1)}\ h$

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But the $\mu_l = \sqrt{3}/2\ \mu_B$ and $\mu_s = \sqrt{3}\ \mu_B$ and it is the spin normally. The condition requires a giromagnetic factor g = 2 for the electron and g = 5.5855 for the nucleus and $\mu_s = \pm 2\ s\ \mu_B$.

If a single electron occupies a p, d or higher orbital, there are both orbital and spin angular moments and according to the rules of wave mechanics these may be combine to give total angular momentum $\sqrt{j(j+1)}$ in two ways. The quantum number j may be either l + s or l – s that is j may be $l \pm 1/2$. The energy of the atom is different for the two values of j.

No two electrons in one atom can have an identical set of quantum numbers, Pauli's exclusion principle. Since two values of s are permitted ($\pm$ 1/2), it follows that the numbers of electrons associated with the various levels are as follows:

s = 2 electrons
p = 6 electrons
d = 10 electrons
f = 14 electrons

12. **Configuration of Many–electron Atoms**

In building up the periodic table by starting with the hydrogen atom and successively adding a proton to the nucleus and an electron to the extranuclear shell (this process is called the Aufbau principle) we must allow for the screening effects evidenced above. In other words, we must account for the fact that orbitals of the same n quantum number but different energetic in a given atom.

– The first empirical rules concerning the order of filling of the hydrogen atom orbitals:

(a) orbital energies increase as (n + 1) increase;
(b) for two orbitals of the same (n + 1), the one with the smaller n lies lower in energy. Thus, the order becomes: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, ...
(n + 1) 1 2 3 4 5
(c) the Hund rules concerning the maximum multiplicity;
(d) the maximum stability for the d or f orbitlas half or total engaged: d^5–d^{10}, f^7–f^{14}
(e) the Pauli principle: two electrons can not have the same quantum numbers; can be electrons with the same n, l, m_l, but different m_s.

The decrease in Z with increasing r is a consequence of the shielding of nuclear charge by the other electron closer to the nucleus and appear an effective nuclear charge (Z*). Figure III. 8. Shows the variation in Z* as a function of r for the third electron of Li.

Figure III. 8.

(a) Z* and Z*/r versus r for the third electron of Li
(b) Surface probability plots for 2s and 2p functions in relation to the same plot for two 1s electrons.

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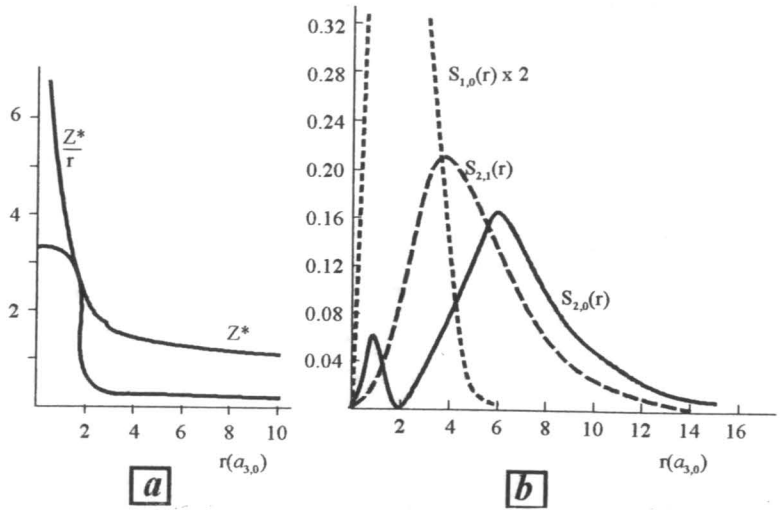

(a) Z*/r is infinitely large at r = 0 and fairly rapidly decrease to a very small value.

A quantitative estimate of the relative energies of outer electrons can be obtained from estimates of their potential energies as given by: $V = -e^2 \cdot Z/r$.

According to the wave formulation of the problem we need to consider the overage potential energy given by:

$$\langle V \rangle = -e^2 \left\langle \frac{Z}{r} \right\rangle = e^2 \int_0^\infty \frac{Z}{r} S(r)\, dr \int_0^\pi \theta(\theta)^2 \sin\theta\, d\theta \int_0^{2\pi} \Phi^*(\Phi)\, \Phi(\Phi)\, d\Phi \approx -e^2 \int_0^\infty \frac{Z}{r} S(r)\, dr$$

From figure III.8. (b) it is readily apparent that both 2s and 2p penetrate the 1s pair charge distribution, the 2p to a seemingly greater extent than the 2s.

A 2s electron penetrates best when (0 to 1.5 a_o) it counts most and realizes a significantly lower energy than a 2p electron. It is no surprise that for Li, the lowest energy configuration for three electrons is $1s^2\ 2s^1$ rather than $1s^2\ 2p^1$. This is a physical basis for the empirical rule that the lower the (n + 1) value for an orbital, the more stable is the orbital.

The second part of the rule deals with the eventuality that (n + 1) is the same for the two orbitals. Such a situation is first encountered with 2p and 3s. That is, will the proper configuration for boron be $1s^2\ 2s^2\ 2p^1$ or $1s^2\ 2s^2\ 3s^1$.

Figure III.9 a. b. c is a series of plots and provide a physical basis for the answer that the lowest energy configuration is $1s^2\ 2s^2\ 2p^1$.

Figure III.9.

(a) Z* and Z*/r versus r for the third valance electron of boron.
(b) Surface probability plots for 2p and 3s functions in relation to the same plot for two 1s and 2s electrons.
(c) The 2p and 3s potential energy curves for Z = 5 with 1s and 2s electron pair present.

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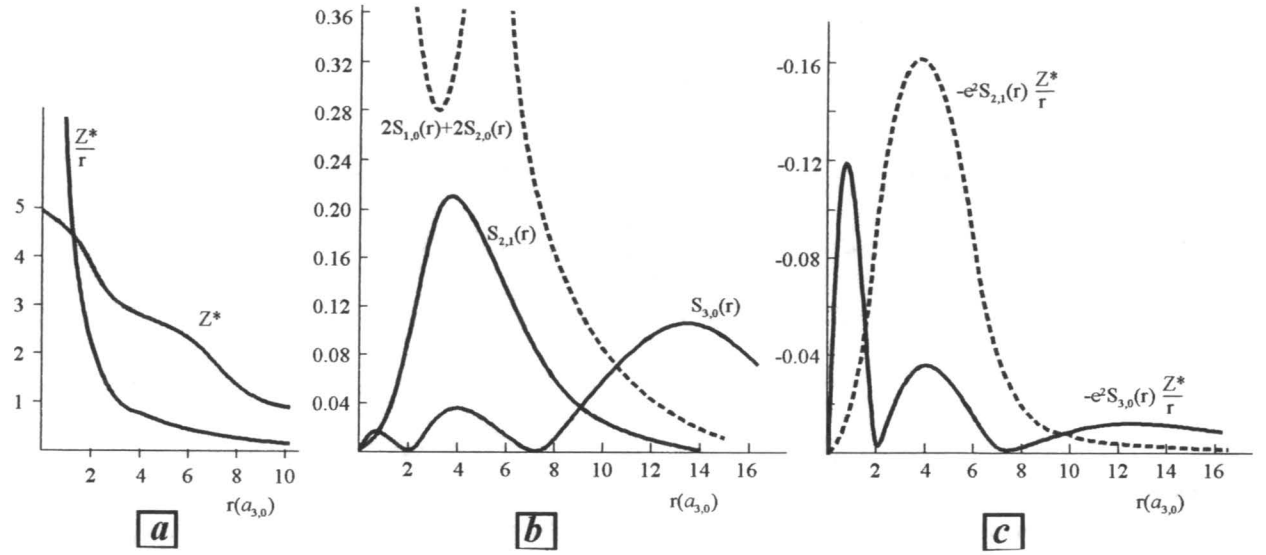
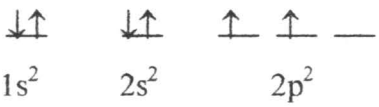


The penetration of the $1s^2\ 2s^2$ core by a 2p electron is for more extensive than that of the 3s electron. Figure III.9 for the 2p orbital provides a lower energy motion for the boron electron than does the 3s orbital.

The physical phenomenon on which the Pauli principle is based is that two particles with the same spin do a better job of avoiding each other in space than do two electrons of opposite spin quantum number. In fact, this phenomenon is a spin – quantum effect and it is observed for any particle that possesses spin angular momentum.

The chemical significance of this correlation of electron motion is that, since electrons are charged and repel one another, the repulsion is less by an amount called the "exchange energy" for electrons of alike spin than for electrons of different spin. In passing from boron to carbon we see this effect. Charge correlation (e^2/r) dictates that a lower energy situation exists if the two p electrons have different angular function. Spin correlation further affords a lower (more negative) energy for alike spins. For carbon the two p electrons reside in different orbitals with the same m_s value.



To summarize, placed two electrons in the same orbital will lead to higher repulsions than if they move in different spatial orbitlas. In addition to the lower energy made possible by allowing separate orbital motions for the two charged particles, the spin correlation allows for a further reduction in repulsion if both have the spin. The stability of p^2 electron arrangement for carbon is:

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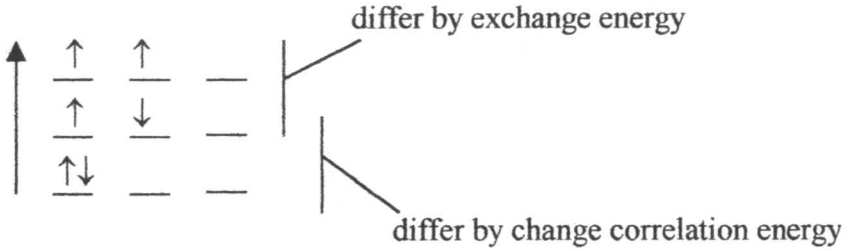
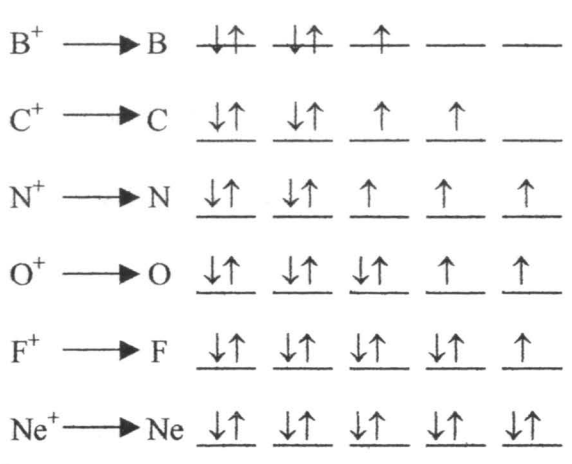


Very often, the electron configuration and energy of an atom are dictated by fine details of electron repulsions that are not apparent in the average repulsion concept of orbital energies.

A good illustration can be found in the trends in ionization potential and electron affinity.

Electron affinity is defined as the energy for the process $atom^- \rightarrow atom + e^-$. For the main groups the valance configurations of these elements are $ns^2\ np^x$, where x = 1, ..., 6. The trend of increasing I and E across this series is broken at the configuration $s^2\ p^4$. The configurations with x = 1, 2, 3 follow a smoothly increasing trend in I as do the configurations x = 4, 5, 6. The origin of the dislocation at $s^2\ p^4$ is easily traced to a discontinuity of electron repulsions, as the nuclear charge smoothly increases by 1 across the entire series.

The following box diagrams should clarify the anomaly:



regularly increasing nuclear charge; regularly increasing electron repulsion;

these electrons do not benefit from the "exchange energy" stabilization possible for the preceding three members of the series and further suffers from larger coulombic repulsion.

Another illustration of the breakdown of the screening concept arises for the transition elements. The orbital energies estimated from shielding or penetration effects adequately account for the fact that the 4s orbital is filled prior to the 3d on passing from Ar to K to Ca. However, proceeding across the 3d series of metals (Sc

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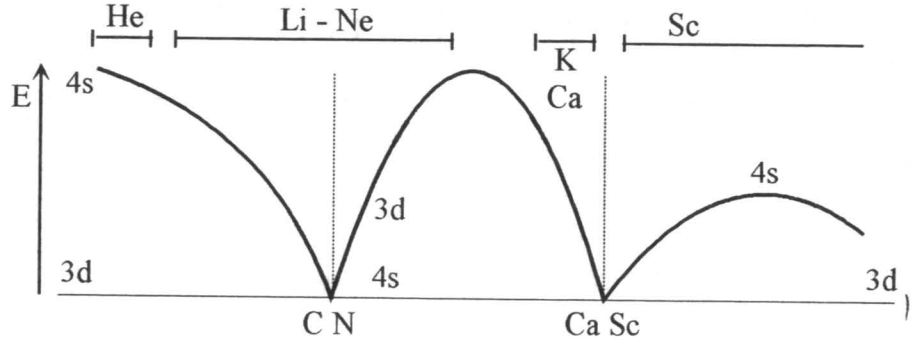
through Zn), there are the so–called anomalies at Cr and Cu, which have [Ar] $4s^1$ $3d^5$ and [Ar] $4s^1$ $3d^{10}$ configurations.

As figure III.10 shows, the relative 3d and 4s orbital energies are:

Figure III.10.

Relative 3d and 4s orbital energies as a function of Z. Reversals occur at the dotted lines.

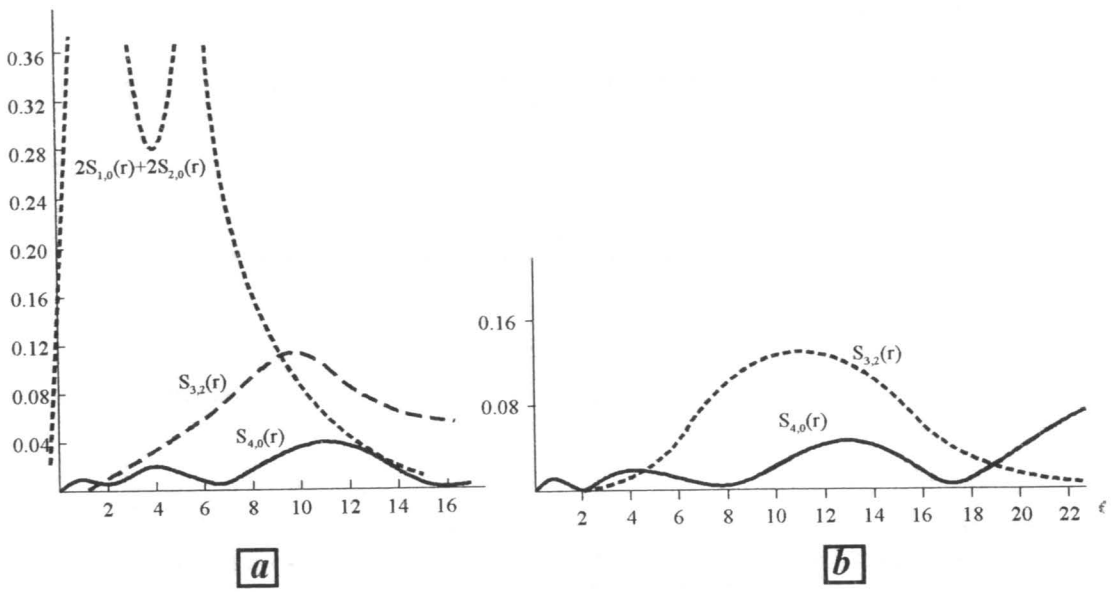


Orbital energies are nearly the same for the first transition elements and under such circumstances the orbital occupancies are as much influenced by the finer points of electron repulsions as by the "orbital energies".

Reference to table 2 show just how complex the situation becomes; of the ten transition metal groups, five show irregularities in electron configuration.

Figure III.11.

The 3d and 4s surface probabilities in relation to the $1s^2$ $2s^2$ core



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Thus while "the stability of half–filled shells" seems a good phrase to invoke for Cr, the "principle" fails for W. It is certainly better to realize that the electron configurations of these elements depend on fine points of electron configurations (the balance between d/d, d/s, s/s repulsions) and accept them for what they are than to propose a rule that must be violated 50% of the time.

In the hydrogen atom, the 4s orbital energy is greater than that of the 3d; yet, by adding six protons to the nucleus and six electrons to the 1s, 2s and 2p orbitals, the 4s moves to lower energy than the 3d. This is easy traced to effect on potential energy of the relative 4s and 3d penetrations of the $1s^2$ $2s^2$ $2p^2$ core of electrons. This penetration is illustrated in figure III.11.a. The stabilization of the 4s relative to the 3d continues throughout the second period. Across the third period, where n = 3 shell begins to fill, the penetration of $3s^x$ $3p^y$ configurations of these elements by the 3d function is much greater than by the 4s, figure III.11.b, with the result that the 3d begins to drop sharply in energy approaching the energy of the 4s at potassium.

Quite obviously, the 3d thoroughly penetrates the 4s function, so as electrons are added to form potassium and calcium, the 3d continues its sharp drop to become as stable as the 4s, or slightly more so at Sc.

While the electron configurations of the transition elements in the zero oxidation states are difficult to intercept, the configurations of the divalent and trivalent ions are much simpler. All di– and trivalent ions of the transition elements have d^n configurations.

For the ions, the energies of the d orbitals are considerably lower than the energies of the next higher s orbital.

Table III.2.

The nd and (n + 1)s configurations for transition elements.

Sc $d^1 s^2$	Ti $d^2 s^2$	V $d^3 s^2$	Cr $d^5 s^1$	Mn $d^5 s^2$	Fe $d^6 s^2$	Co $d^7 s^2$	Ni $d^8 s^2$	Cu $d^{10} s^1$	Zn $d^{10} s^2$
Y $d^1 s^2$	Zr $d^2 s^2$	Nb $d^4 s^1$	Mo $d^5 s^1$	Tc $d^5 s^2$	Ru $d^7 s^1$	Rh $d^8 s^1$	Pd $d^{10} s^0$	Ag $d^{10} s^1$	Cd $d^{10} s^2$
La $d^1 s^2$	Hf $d^2 s^2$	Ta $d^3 s^2$	W $d^4 s^2$	Re $d^5 s^2$	Os $d^6 s^2$	Ir $d^7 s^2$	Pt $d^9 s^1$	Au $d^{10} s^1$	Hg $d^{10} s^2$

Summarizing, all elements in the main group have the same valance orbital configuration. This is not always true for the transition elements. Ionization of the representative elements results in ions that appear to have simply lost the least stable electrons in the valance shell.

For the transition ions, the electron configurations are those to be expected because the orbital are clearly more stable than the s orbitals of one greater quantum number, n.

Using the potassium–copper pair as an example both have $4s^1$ valance configuration, but this electron potassium is outside a $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ core that 4s

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electron does not penetrate as well as the 4s electron of copper penetrates the $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ core of that atom.

The 10 extra d electrons of copper do not completely screen the additional 10 units of nuclear charge. Clearly, the loss of an electron (the 4s) from potassium should require much less energy than from copper.

Thus, the correlation between valance configuration and group in the periodic table is not perfect (hence the use of A and B groups in the long form of the periodic table) but at least it is understandable in terms of the hydrogen radial functions.

One more consequence of orbital penetration is orbital contraction. The greater the orbital penetration of core electrons, the greater will be the contraction of the orbital function – that is, the maximum in the probability curve will occur at a smaller distance from the nucleus and the wave amplitude (electron probability) will increase at small r and decrease at large r. This phenomenon is of some importance in interpretations of atom hybridization.

13. **Slater Orbitals and Their Uses**

Slater put the concept of orbital penetration and electron screening on a more quantitative basis and developed a method for approximating the radial functions for real atoms by assuming that only the highest–order term of each Schrödinger radial function is important. The radial function is:

$$R(r) = N_r \cdot r^{n^*-1} \cdot e^{-(Z^*/n^*)r}$$

N_r: a normalizing constant that is different for different orbitals (it depends on Z* and n*).

These functions are quite a bit different from the hydrogen atom solutions, in that they do not depend explicitly on the l quantum number (2s and 2p have the same radial function) and they all have only one mode, which occurs at $r = 0$.

Slater's approximate functions poorly mimic an electron's behavior in the inner regions of the atom. It is found that his functions are very similar to the correct functions from the nucleus in the range of covalent bond distance. Thus, they have been useful for calculations of bonding between atoms in molecules.

Slater's rules pertain to prescription of values of Z* and n* to be used for the various atomic orbitals. Slater used his functions to calculate the energies of a large number and found for each atom the values Z* and n* of that gave the best agreement with experimental values. Then, by inspection, he determined a simplified set of rules that would yield Z* and n* values near these optimum values.

Rule 1: orbitals are grouped in the following manner:

(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p)

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Rule 2: the effective atomic number for each orbital group is determined by the actual atomic number decreased by a certain amount (the screening constant, s_i) for each electron in the same or preceding groups.

$$Z^* = Z - \sum_i s_i$$

Electrons in following groups have screening ability according to this approximate scheme.

Rule 3: each electron in a group screens 0.35 nuclear charge unit ($s_i = 0.35$) from all other electrons in the same group – except for a 1s electron screening another 1s where the screening is reduced to 0.30.

Rule 4: when calculating Z* for a d or f group electron, each electron in all preceding groups screens 1.00 charge unit. For (ns, p) group electrons, each electron in the group n' = n – 1 screens only 0.85 charge unit; all electrons in further preceding groups screen 1.00 unit.

Rule 5: values of n* are not the same as n for larger n:

n	=	1,	2,	3,	4, 5, 6
n*	=	1,	2,	3,	3.7, 4.0, 4.2

	s_i for electrons in			
Electron group	All higher groups	Same group	Groups with n' = n – 1	Groups with n' < n – 1
(1s)	0	0.30		
(ns, p)	0	0.35	0.85	1.00
(nd), (nf)	0	0.35	1.00	1.00

A useful consequence of Slater's "average repulsion" model is that for a series of elements with the same (ns, p) or (nd) group electrons, Z* regularly increases by 0.65.

The model suggests, then, that atomic properties should smoothly vary from one element to the next. Slater's functions can be used to calculate the energies of atoms and ions and their radii with some success. The energy of the atom or ion is proportional to the sum of the $(Z^*/n^*)^2$ for each electron in the last group. This radii can be estimated from the maximum radial charge density for the electrons in the last group. This maximum occurs at (n^{*2}/Z^*) atomic units.

To illustrate the application of Slater's rules, we will calculate the ionizations potentials of Li and F. The lithium atom has the configurations $1s^2\ 2s^1$ and the ion has $1s^2$.

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The first ionization potentials is just the difference in energy between the +1 ion and the atom:

$$I = E_{Li}^{+} - E_{Li}^{0}$$

To calculate the energies of the ion and atom, we sum the energies of their electrons as given by $-13.6\ (Z^*/n^*)^2$ (units of electron volts). Since the 2s electron of the atom is presumed not to screen nuclear charge from the 1s electrons, the energies of 1s electrons will be the same in the atom and in the ion.

In this case the ionization potential is simply the energy of the 2s electron in the atom.

$$I = -13.6[\{2(Z^*/n^*)^2_{1s}\}_{ion} - \{2(Z^*/n^*)^2_{1s} + (Z^*/n^*)^2_{2sp}\}_{atom}] = +13.6(Z^*/n^*)^2_{2sp}$$

Since each of the two 1s electrons of the atom screens 0.85 charge unit from the 2s electron,

$$Z^* = Z - 2 \cdot (0.85) = 1.30.$$

The calculated ionization potential for Li is therefore 5.8 eV to be compared with an experimental value of 5.4 eV.

For the fluorine atom, the calculation is similar. The ionization potential is the difference between the ion and atom energies. The atom has the configuration $1s^2\ 2s^2\ 2p^5$ or $(1s)^2\ (2\ sp)^7$, while the ion has the configuration $(1s)^2\ (2\ sp)^6$. Again, since the 1s electrons "see" the same nuclear charge before and after ionization, their contributions to the energies of the atom and ion are the same and will cancel when the difference is taken. The ionization potential is:

$$I = -13.6[\{6(Z^*/n^*)^2_{2sp}\}_{ion} - \{7(Z^*/n^*)^2_{2sp}\}_{atom}]$$

Since Z^* far the 2 sp group before ionization is different from that after ionization (there is a charge in the number of electron in the group, so the energies of the remaining electrons change), we must compute Z^* for the 2 sp group both in the ion and in the atom. In the ion there are two (1s) group electrons and five (2 sp) electron and the effective nuclear charge for any one of the (2 sp) electrons, is

$$Z^* = Z - 5 \cdot (0.35) - 2 \cdot (0.85) = 5.55.$$

For the atom, there are two (1s) and six (2 sp) electrons and

$$Z^* = Z - 6 \cdot (0.35) - 2 \cdot (0.85) = 5.20.$$

The calculated ionization potential for fluorine is 15 eV, to be compared with the experimental value of 17 eV.

The agreement of these calculated values with experiment is typical; the error is on the order of 10%. This prevents the approximate method from being quantitative, but it is never the less useful for estimates. More accurate results can be obtained by sacrificing the simplicity and the minimum number of rules in Slater's prescription of Z^*.

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Types of nuclei

The nucleus occupies 10^{-15} from the atom volume and has a diameter of ~10^{-12}-10^{-13}, but it has a very high density ~10^{12}-10^{15} gr/cm^3 and also a very big positive charge density ~5 10^{18} C/cm^{3E}E E. Rutherford (1911) and Moseley (1914) studied the evolution of the nucleus. Rutherford appreciated that the volume of the nucleus in rapport with that of the entire atom is a multiple integer of elementary charges and it characterizes the atom for one element.

After the emission atomic spectrum, from X-ray domain, Moseley found that the lines are dependent on this relation:

$$\sqrt{\nu} = K(Z-a)$$

were ν is the frequency of one line from the spectra

- K-is the proportionality constant for all the lines
- Z-the atomic number of the element.

For the constant K from Moseley's relation we can write:

$$K^2 = \frac{2\pi e^4}{h} \cdot \frac{Mm}{M+m}\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right)$$

M and m being the nucleus mass and the electron mass and leads to the following expression:

$$\nu' = \frac{2\pi^2 e^4}{hc} \cdot \frac{Mm}{M+m}(Z-a)^2\left(\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right)$$

for all the lines of the atom emission spectra.

In this way, both relations represent the same mechanism for producing spectra lines, through electronic transmitions between the energetic levels in the atom, but very far from the visible domain of the spectra, because the frequency increases by four the atomic number.

Thus, for the Zr atom Z=40 a certain line would have the frequency 1600 times bigger than it's analogous line from the hydrogen spectrum, as an effect of the Z^2 factor. In fact, this effect is weakened by the screening action exercited by the electron. This screening is represented by the constant 'a' from Moseley's relation, and by σ from Slater's equation.

A very important step in the knowledge of the electrons was the discover of the neutron (J. Chadwick). On this base, today we know that the atomic nuclei are composed from protons and neutrons. The total number of this subatomic particles, called together nucleons, is given by the mass number A and the number of protons in the same time with the number of the positive elementary charges, characterizes the atom through the order number Z. This relation gives the number of neutrons N from the nucleus: N= A – Z

In the nucleus of the hydrogen atom N = 0; in the other atoms, the number of neutrons is equal or higher than Z.

There are some atomic species, the atoms of the same element, with the same Z, which differ from eachother through A, called by Soddy (1012) isotopes. There are some atoms with different Z and same A, called isobars.

The atomic species with a different Z but the same number of neutrons are called isotones. In order to show the nuclear species we use the symbols of the elements that we write in the down left

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the order number and up the atomic mass A. Like in this element: ${}^{12}_{6}C$ that is the atomic specie of the carbon element with 12 nucleons from which 6 are protons and 6 neutrons.

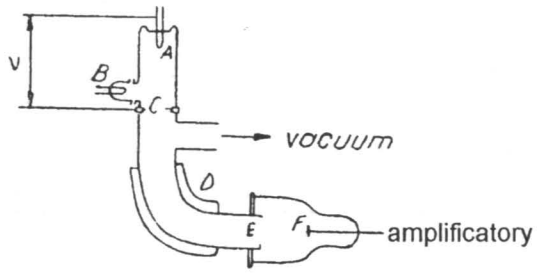

Figure 1. Mass spectrometric apparatus scheme

This specie is the 12 isotope of the carbon. Another specie of carbon is the isotope 14: ${}^{14}_{6}C$ with more neutrons in the nucleus.

The elements ${}^{14}_{6}C$ and ${}^{14}_{7}N$ are isobars, like ${}^{32}_{14}Si$ and ${}^{32}_{15}P$, ${}^{32}_{16}S$ and ${}^{11}_{5}B$, ${}^{12}_{6}C$ and ${}^{13}_{7}N$ with 6 neutrons each in their nuclei are isotones, like ${}^{18}_{8}O$,${}^{19}_{9}F$,${}^{20}_{10}Ne$ with 10 neutrons in the nuclei.

The separation of the isotopes was initiated by Aston (1919) with the mass spectrograph based on the registration of the deviation produced by a magnetic and electric fields over some particles with different masses. In the figure below is the schedule of the functioning principle of the spectrograph.

From the metallic incandescent filament A atoms are vaporized and then ionized through bombarding with electrons from a source B.

A difference of potential V is established between A and a slit C accelerates the ions passing through, with a velocity v cm/S, so we have:

$$\frac{1}{2}mv^2 = Ve$$

wher m is the mass of the ion in g and e is the charge in u.e.s.

The positive ions fascicle, maintained with a pomp at a pressure equal with 10^{-4}-10^{-10} mm, passes in the tube D were is undergone to the action of a magnetic field of intensity H. The moving ion will describe a circle with the radius resulted from the centrifugal force equilibration $\frac{mv^2}{r}$ with the force Hev produced by the magnetic field:

$$\frac{mv^2}{r} = Hev$$

Eliminating v^2 we obtain : $\frac{m}{e} = \frac{r^2H^2}{2v}$

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If we accelerate under the same potential difference V, a fascicle of positive ions with different masses and then we will undergo it to a constant magnetic field than it will separate into distinct fascicles.

By giving to V different successive values we can make that through a slit E of the apparatus, different isotopic fascicle to go to the F plate. In the diagram is presented the current intensity of isotopic ions.

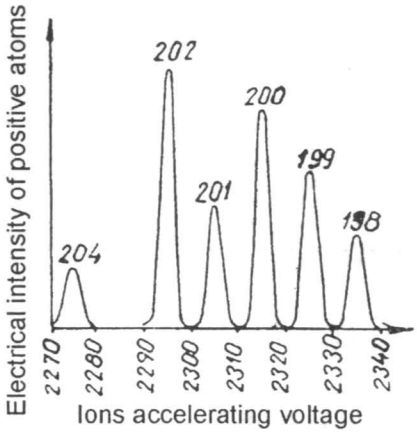

Figure 2. Mercury mass spectrum

The chemical properties of the isotopes for an element are identically but the physical ones are different because of the ratio between their atomic masses.

For separating isotopes some installations are used and a few number of methods:

1.Gasous diffusion. Gases have different densities, ρ diffuses with different v velocities:

$$\frac{v_1}{v_{11}} = \sqrt{\frac{M_I}{M_I}} = \sqrt{\frac{\rho_{II}}{\rho_I}}$$

With this method ${}^{235}_{1}U$ is separated from its natural mixture.

2. Thermal Diffusion. By taking a gas through a vertically tub with cold walls in which an incandescent wire is present, the light isotopic component concentrates on the wire and produces an ascendant current and the heavy isotopic component goes to the walls in an descendent current.

3. Electromagnetic Method. Uses the mass spectrograph principle and it permits the separation of about 200 isotopes.

4. Centrifugal Process. The heavy molecules tend to go to the periphery of the centrifuge to create a descendent current and the light ones go to the axis of the centrifuge in a descendent current.

5. Molecular Distillation. The velocities of evaporating of isotopic components are inverse proportional with the squared of their molecular masses. At distillation the condenser has more light isotopic components.

6. The Chromatography in gaseous state: permits the separation of some gaseous isotopic mixtures using the differences of absorption on same substances.

7. Chancing reactions. The differences between isotopes masses of some elements can be used in chemical selections of isotopes.

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Nuclear Models

The experience shows that the atomic nuclei are spherical, with a radius r that increases with the mass number like:

$$R = r_o \sqrt[3]{A}$$

r_0 being a constant. From this relation we see that the volume of the nucleus increases proportionally with A and the nuclei density is the same as a ratio between the nucleons density. But the density of a nucleus I not constant, it decreases exponentially from the center to periphery, meaning that the nucleus is not limited on a certain surface. The value $r_0=1.1 \cdot 10^{-13}$ cm represents the radius for which the density decreases at half in comparison with the value in the center of the nucleus.

If the volume of the nucleus is delimited through the capacity of the nucleus to catch new nucleons, a bigger value is reached for $r_0=1.4\text{-}1.5\ 10^{-13}$ cm.

On the other side, the existence of protons and neutrons is not proved experimentally meaning that the positive charges could spread on all the nucleons like the electronic cloud from the atomic shell. This delocalization of the positive charges on all the nucleons leaded to the theory of intranuclear attraction forces formation, that explains the coersion between the neutral particles and that positively charged that form the nucleus. The nuclear attraction forces are exchange forces, because which the nucleons charge their character, with a frequency of $\sim 10^{16}$ s^{-1} through the transition of positive charges from one nucleon to another.

Characteristic to these forces is their action only at the direct contact between the nucleons that is to extremely small distances. Also these forces are extremely high, the highest known.

The positive electric charge that migrates from one nucleon to another is a mezoic cloud of charge equal to the elementary unit.

Such mesons were obtained free by bombarding the nuclei with particles with high energies. This fragments of nucleons have intermediary masses between the nucleon mass and the electron mass. It is remarked that if the nucleonic mass fragmentation, the elementary charge fragmentation was possible.

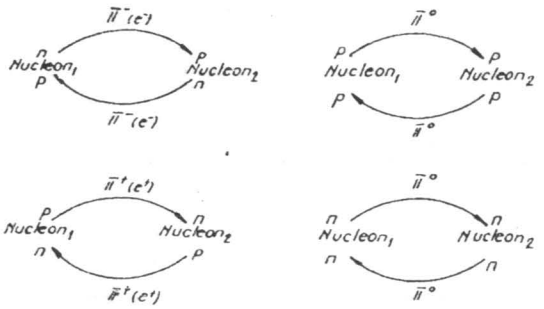

Figure 3. Exchanges forces scheme between two nucleons using π^o, π^- and π^+ mesons transfer

The big number of known subatomic particles confirm the fact a particle can be neutral or charged with an elementary total charge.

The Mechanic-Quantic Description of the Nucleus

The nucleons from a nucleus can be described through their crepuscular aspect of through the ondulatory one. At the nuclear level, the solution of Schrodinger equation correspond to some

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"nuclear orbitals" and to some probability densities for the distribution of the nucleons in nuclear space. The general characterization of the nucleons is done using quantum number n, l, s, j with the same values as for the electrons.

The energetically levels from the nucleus, differ from the electronically ones. The size order 10^6 eV shows that the intensity of the nuclear forces is higher than that of the electrostatic forces between the nuclei and the electrons. The successively order of the layers is different from that of the electronic layers.

We can follow easily the number of free places for the protons and neutrons, in function of n and l, if we denote the layer successively with n=1,2,3..., and the sublyers with l=0,1,2,...n-1.

In an n layer from the nuclear shell, the completion of the l substratum is made in the inverse energetically layer, starting with n-1 and continuing with n-3 , n-5 etc . until 1 or 0. Like this the first layer has 1s level and the second layer 2p, the third 3d and 3s etc. Generally for n add the obtained stratums contained are that ones with even l, and for even n the substratum have odd values for l.

In a substratum l we have 2(2n+1) nucleons. The table shows that in the left side this sequence of energetic levels in function of n and l. The completion of the nuclear layers should correspond to the number of protons and neutron. From the table we see that this is verified only for the first three numbers 2, 8, 20 because the following ones 40, 70, don't correspond to the stabile nuclear configurations.

The explication of the stability for other number of nucleons is found in the electronic shell in the energetic interpolation of some levels from different layers. At the electronic shell there are stabile configuration with the unoccupied sublayers.

Let's examine some nucleons interactions, similar to the electronic ones. The neutrons and the protons like the electrons, couple by spin-spin couple with the same quantum number s=$\frac{1}{2}$. On the other side, the nucleons have orbital magnetic moments too and it results that spin-orbital couple is possible. The contribution of the stability of the two types of coupling has a very big importance for the stability of the two energetic phases from the nucleus, but inverse than that of the stability of electronic shell. While the spin intensity has a small value of Bohr magnetic momentum, the nuclear spin has a 2000 times smaller value: ${}^1\mu_B = \frac{eh}{4\pi m_e c}$: ${}^1\mu_N = \frac{eh}{4\pi m_p c}$

The nuclear spin is neglected in comparison to the electronic spin. The couple nuclear spin-orbital is very important because of the characterization of the energetic states of the atomic nucleus. It was found that for the nucleons from a layer in number of 2(2l+1) as a result of nuclear spin-orbital coupling is produced a difference, and a energetically change in nucleus corresponding to the intern quantum number j defined: j=l $\pm s = l \pm \frac{1}{2}$

The more stabile level corresponds to the value l+$\frac{1}{2}$ and the highest one less stabile, to the value l-$\frac{1}{2}$. The energetic difference is of MeV order.

The number of free places is given by the intern quantum number and is equal to 2j+1 states.

From the table we observe for example that the level l=3 from the fourth layer is divided in j=3+$\frac{1}{2}=\frac{7}{2}$ and in j=3-$\frac{1}{2}=\frac{5}{2}$. The more stabile energetically level is decreased by 5 MeV in

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comparison with 0.5 MeV on the highest level from the level 3, such that by completing with $2 \cdot \frac{7}{2} + 1$ nucleons, a new nuclear configuration appears.

For some time now, some nuclear species of the some elements are known. They have the same number of neutrons, but they differ between them through the fact that they emmmit or not Gamma-rays of small energy and intensity. This species are known as isomers. The phenomenon of nuclear isomerism is applied by the excited states of the nuclei that get unexcited slowly.

The layered structure of the nucleus explains a part of its behavior than can be found also in the electronic structure. The quantum nuclear states generate a quantum field for the satellite electrons that succeed on the permitted energy levels in the atomic field of the atom. We can say that the same conception leads us in the interpretation of the nuclear phenomenon.

The nuclear spin, generated by a proton or an electron from the nucleus, interacts with the magnetic field of the electrons from the atomic shell producing a resultant, important source of informations about the structure of the chemical compounds. On another side through the non-homogenous electrostatic field generated by same nuclei, the electronic shell is influenced, such that we can draw a conclusion about the influence of the nuclear cloud upon the chemical bond.

Magnetic and Electronic Nuclear Magnetic Interactions

1. NMR Spectra. The Nucleus orientation in the Magnetic Field

The nuclear magnetism generates interactions with the electronic shell, being an important source of information for the structures of the substances.

A nucleus manifests magnetism if it has an odd proton or an odd neutron. Even if the nucleonic spin has the same values, the coupling takes place only between the nucleons of the same type.

So, if ${}_{1}^{1}H$ and ${}_{2}^{3}He$ have a total magnetic momentum of $I = j = s = \frac{1}{2}$, because in the atomic hydrogen the neutron generates the nuclear spin, but in ${}_{1}^{2}H$ or in ${}_{7}^{14}N$ then is a proton and neutron unpaired that sum their magnetic moments and we have I = 1.

The total momentum can be zero, with it's maximum value $I = \frac{9}{2}$. Generally the I dependence on Z and N results from the table below:

Table 1. Total nuclear magnetic moment function of Z and N

Z	N = A – Z	I	Example	
odd	odd	zero	${}_{6}^{12}C$	${}_{8}^{16}O$
odd	even	semi-integer	${}_{6}^{13}C$	${}_{8}^{17}O$
even	odd	semi-integer	${}_{9}^{19}F$	${}_{19}^{39}K$
even	even	integer	${}_{3}^{6}Li$	${}_{5}^{10}B$

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About the effective value I different from zero, we can find that out easily from the table from which we can write in which level we can find the non-paired nuclei for which $I = j = l \pm \frac{1}{2}$. Some typical examples we find the next table:

Values of nuclear magnetic moments

Nuclide	Nonpair nucleon	Position level	n	I
${}^{2}_{1}H$	proton, neutron	0 + 1/2+1/2	1	1
${}^{13}_{6}C$	neutron	0 – 1/2	2	1/2
${}^{17}_{8}O$	neutron	2 + 1/2	3	5/2
${}^{31}_{15}P$	proton	0 + 1/2	3	1/2
${}^{35}_{17}Cl$	proton	2 – 1/2	3	3/2
${}^{37}_{17}Cl$	proton	2 – 1/2	3	3/2
${}^{39}_{19}K$	proton	2 – 1/2	3	3/2
${}^{83}_{36}Kr$	neutron	4 + 1/2	5	9/2
${}^{121}_{51}Sb$	proton	2 + 1/2	5	5/2
${}^{205}_{81}Tl$	proton	5 + 1/2	6	11/2
${}^{209}_{83}Bi$	proton	5 – 1/2	6	9/2

Knowing the value of I of the nuclei that manifest magnetism is very important in the interpretation of the magnetic behavior in the exterior magnetic field. It offers some information over some chemical structures of the substances that have such nuclei.

In the absence of an exterior magnetic field the orientation of the nuclear magnetic moments μ_N is negligible; a degeneration state appear from the point of view of the rotation axis orientation of the nucleus itself. The degeneration is suprimmed if on exterior magnetic field H_m is applied.

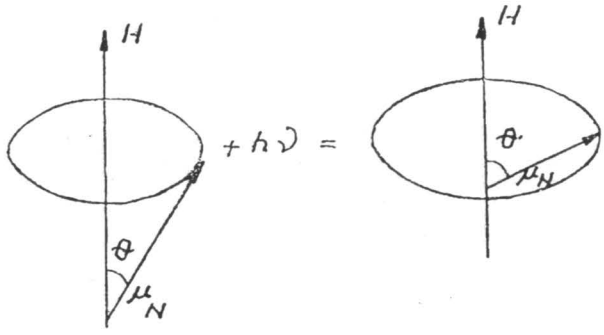

Figure 4. Excitation of nucleus

In the same situation, the nuclear magnetic momentum will perform an angle θ with the direction of the exterior field.

The value of the angle determines the potential energy of the nucleus in its different possibilities orientations $-\mu_N H_m \cos\theta$.

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The value of the angle θ cannot be neglected. The permitted orientations are only those with a definite orientation through the magnetic quantum number from the ratio:

$$\frac{mh}{2\pi}$$

were m has the values: I, I-1, ...0, ...-(I-1), -I, meaning 2I+1 values.

Different nuclei have different energies depending on their orientation in rapport with the field and the energy changing takes place by following the rule of selection:

$$\Delta_m = \pm 1$$

If we represent the nuclear magnet as a vector μ_N that has a precision moment around the Hm field then, the excitation, the energy absorption we can describe it through the increasing of the angle.

The measure order of the energy implicated in such process can be deduced from the quanta frequency that results from:

$$\upsilon = \frac{\mu_N Hm}{Ih}$$

Hm being of 10^3-10^4 gauss order, μ_N of order 10^{24} erg-gauss^{-1} and h of 10^{-27} ergS and I being without dimensions results:

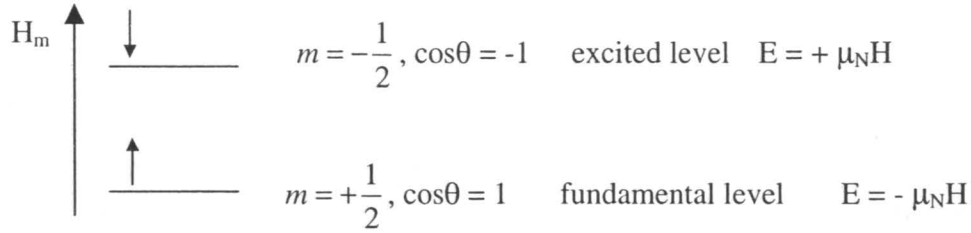
$$\upsilon = \frac{(10^3 - 10^4) gauss \cdot 10^{-24} erggauss^{-1}}{10^{-27} ergS} \sim 10^6 - 10^7 S^{-1}$$

This measure order places ν in the ratio frequency domain from the electromagnetic spectra.

Let's examine the possibilities offered for the nuclei orientation ${}_1^1H, {}_9^{19}F, {}_{15}^{31}P$, in the most frequent and simple cases, for which I=1/2. In these cases there are m = 2I + 1 = 2 possibilities of orientation and they are:

1. for $\theta=0^0$ and
2. for $\theta=180^0$.

The superior energy state is that one for which the nuclear magnet is orientated antiparallel with the field where m=-1/2 and the fundamental state of the lowest energy of the nuclear magnet parallel with the exterior field for which m= +1/2. By using the arrows for the relative orientation we can draw the two energetically states of the nucleus like this:



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From this scheme we can see that the energy displacement of both levels increases with the field intensity H. Because bigger intensities than 10^4 gauss are hard to obtain, the excitation, consisting in this base, in the nuclear spin inversion in rapport with the field, implies radiant energies from the radio frequencies domain, much smaller than the thermal energy agitation corresponding to infrared region from the electromagnetic spectrum.

The probability to find the nuclei in the fundamental state is higher than that of finding them in excited at the substance irradiation with energy quanta hν and prevails the absorption. This fact can be registered experimentally. The absorption in these conditions is a resonance phenomenon, called nuclear magnetic resonance (NMR) because it implies energies of some nuclear magnetons unities order.

From the scheme we also can observe that the absorbed energy is: $\Delta E=h\nu=2\mu_N H$

The magnetic field H from around the nucleus is not the same with the exterior applied magnetic field H_m because, until it reaches to act upon the nucleus its value is modified because of some interactions,

1.the magnetic moment action generated by the electronic shell from around the nucleus, which we denote by He

2.the action of neighboring nuclei from a solid with the total moment denoted by Hs.

This effect Hs is annihilated in liquids and in gasses because of the thermal agitation

3. the action of neighboring nuclei from the molecule or the polyatomic ion, that generates magnetic field Hn, which has an intensity that modifies upon the electronic shell. This action is dependent on the intensity Hm of the exterior applied field and on the molecular thermal agitation, but is not independent on the fact that suppresses the rigidity of the molecular thermal building.

The effective field H, which acts upon the nucleus where the resonance is produced, is the resultant of all the interactions enumerated: H= Hm + He + Hs + Hn

In this sum the terms succeed decreasing as dimension order.

Each of the three terms that represent the proper magnetic effects of the substance; He, Hs and Hn give important informations for the knowledge of some structural details of the substance, as we will show.

The nuclear magnetic resonance would be produced in two ways; because upon the nucleus simultaneously act the exterior magnetic field Hm and the radio waves hν. If we use a radiant constant the intensity of the exterior magnetic field Hm, by the modification of the frequency we reached a particular value for which the resonance absorption produced. If we use a radiation source of constant frequency then to bring out the resonance we must modify the field intensity Hm. In practice, the last one is more convenient. It is realized if to a magnet or an hard electromagnet of a static field of $H_0=10^4$ gauss, a supplementary spire device id applied that can modify the initial intensity of the field with an integer number of ΔH, ~20 gauss, we have:

$$Hm = H_0 \pm n\Delta H = H_0 \pm n$$

The graphical representation of the resonance curves have in their abscise the increasing of ΔH and on the ordinate the resonance absorption intensity. The curves of the magnetic nuclear resonance shapes are placed between the two extremes. One corresponds to the given spectrum of isolated nuclei and the other one to the spectrum of the nuclei being in a solid lattice of a medium with similar nuclei. The isolated nuclei give in the spectrum of resonance curves with maximum intensity and extremely width and for a solid plate and extended curves are registered:

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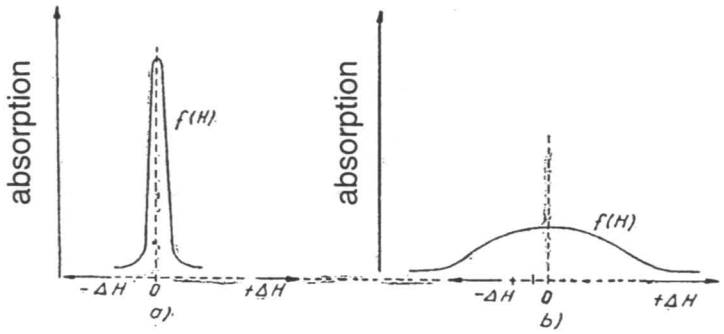

Figure 5. NMR curve form

a – of an isolate nucleus, b – of an nucleus surrounded by similar nucleuses in solid state

NMR Applications in Chemistry

1.The calculus of the internuclear distances in solids.

Some applications of the NMR spectrum are very important in chemistry. The NMR spectrum of the isolated nuclei are not that important for the chemists but the ones given by the solid substances are very important for the calculus of some internuclear substances.

The absorption curve reflects the extension and the distances that separate the nuclei. It is demonstrated that the length of the absorption is proportional with $1/d^3$, d being the internuclear distance. Even if the calculus is complicated the results have a higer precision than the diffraction X methods electrons diffraction and even than the neutrons diffraction. So, the internuclear distance $d_{N\text{-}H}$ in NH_4Cl is calculated as being 1.038±0.004 A from NMR dates, and in the same time those from the neutron diffraction method d_{NH}=1.03±0.2A.

1. The determination of the molecular structure

In the solids, the nuclei with magnetic momentum being too far from each other the interactions are so weak that Hs is neglected. In these cases, He becomes very important. The ratio He/Hm is characteristic for a particular environment in the molecule. In the resonance curve we have the possibility to follow the variation of He/Hn 10^6, called chemical displacement upon the reference structure with a given environment. The chemical displacement gives us the possibility to see and to identify the difference between some environments functional groups from a molecule around the examined nucleus.

A particular case is of the phosphoric ions, diphospate and tryphosphat with their magnetic resonance curves for ${}^{21}_{15}P, {}^{31}_{15}P$ similar with that from the figure.

The interpretation of these curves is:

The curve 1: the spatial diphosphate has the two atoms of P in the same spatial arrangement, both having the endings of the smaller chain possible. Thou, the curve has only one resonance signal.

The curve 2: The tryphosphate ion beside the P atoms it has also another one with two atoms of 0 points.

As a consequence the second reference signal appears chemically displaced in comparison with the first one. Because He_1 of the P atom is different than the He corresponding to the marginal atoms.

The intensity of the second signal is half from the reference signal, as a consequence of the fact that the number of P atoms that produces this signal is half of the number of margined atoms.

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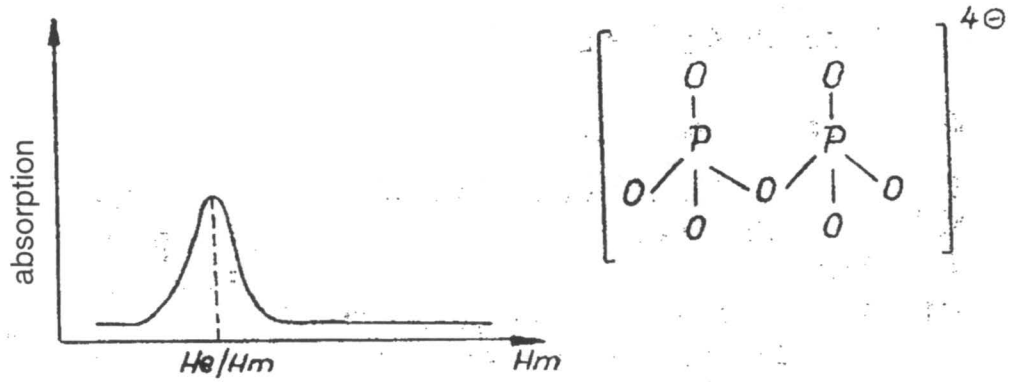
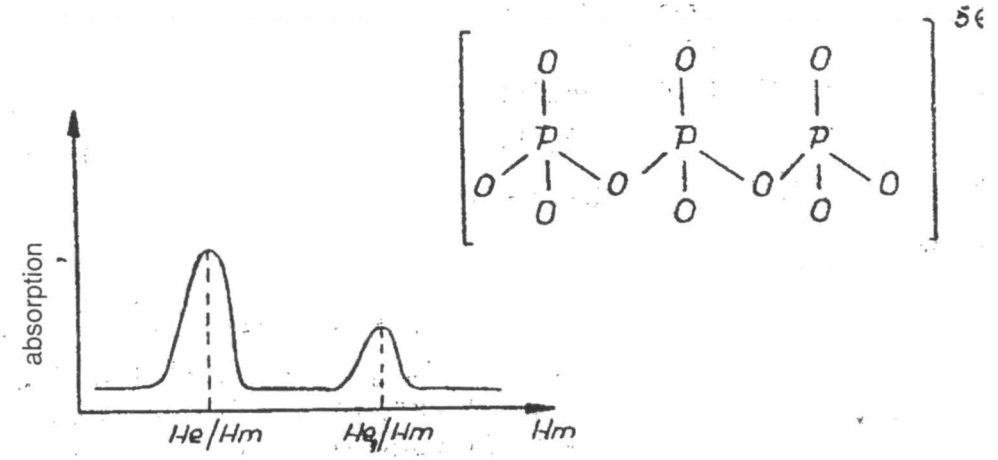
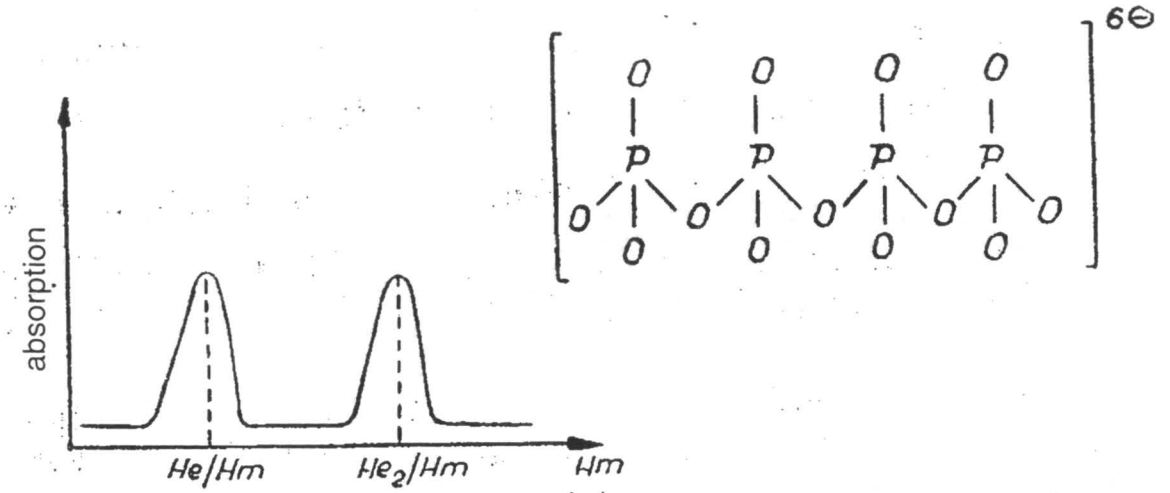


1) Resonance curve of diphosphat ion (single signal)



2) Resonance curve of diphosphat ion (two signals)



3) Resonance curve of tetrahosphat ion (two signals)

Figure 6. $^{31}_{15}P$ NMR resonance curve of first three polyphosphats

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The curve 3: tetraphosphate ion with the rapport Pmargnal/Pcentral=1 is characterized by two signals of equal intensity.

Into another example of the ethanol we distinguish on the NMR spectrum curve ${}^{1}_{1}H$ of the proton there signals in rapport to the intensity 3:2:1.

As we can see the number of signals from a NMR curve gives us informations about the number of environment types,

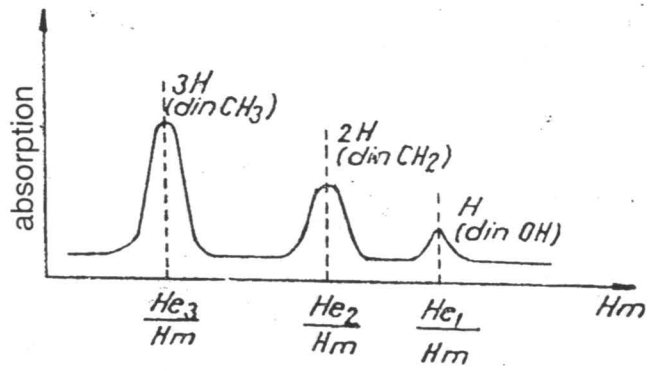

Figure 7. ${}^{1}_{1}H$ NMR resonance curve of ethanol

that can be found around the atom. Their relative intensities of the signals are in the same rapport as the relative number of atoms from each type of environment.

The Magnetic Internuclear Influences and
Their Importance for the Structural Interpretation

As we saw, into a solid there are many interactions between the neighboring nuclei and they have magnetically properties, like in between the nuclei and electronic shell of their atoms. The resonance signal becomes in this condition a curve with significant breadth.

The nature of the interactions can be understood if we follow what happens when some nuclei being under the influence of other small molecules, where the interactions are limited. The simplest example is the H_2 molecule. Each proton from the molecule manifests a nuclear magnetism. Into a variable magnetic field, Hm is obtained a resonance signal at the absorption of quanta energy when the spin is inversed in rapport with the field orientation. Hn determines the effective magnetic field H, a resonance phenomenon is produced too, generated in this case by the partner proton from the molecule. There are two possible situations: the partner protons to have the same spin or of contrary sense with that of the proton that suffers the transition. At the o-hydrogen the absorbed energy for the resonance and that by spin inversation transforms it to p-hydrogen is smaller than the energy needed for the resonance obtaining into the isolated atom, because at the atomic hydrogen the magnetic field of the second atoms is missing. This if it has the spin of the same sense, lightens the transitions by the energy excess represented by the reciprocally repealing. But, if the resonance is produced in p-hydrogen the transition needs more energy than for the isolated H atom, because it has to absorb the energy needed for the nuclear spin decoupling.

In the resonance curve of the molecular hydrogen at low temperature the resonance signal is spitted into a doublet. The same intensity of the doublet compounds, same length shows that the o-p and p-o transitions are equally produced. The doublet makes the fine structure would not appear for higher temperature when the compounds join together into a single signal.

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A similar splitting is produced in the case of pirophosphat ion too, at low temperature.

A more complicated example is the mixed molecule H-D. For the H atom from the molecule the magnetic momentum is I=S=1/2 and for ${}_1^2D$ this has the value I = 2S = 1. The D nucleus is exactly in the same situation as the proton from the H_2 molecule meaning that it can surprise the proton at the transition even with the parallel spin even with the antiparallel spin, which inverts from the D nucleus. The resonance sign of the proton is much complicated, because in the D nucleus there is a nuclear spin owed to the proton and to the neutron their orientations being of the same probability.

When the proton suffers the transition at the resonance the D nuclei can be found in the following situations regarding the spin orientation:

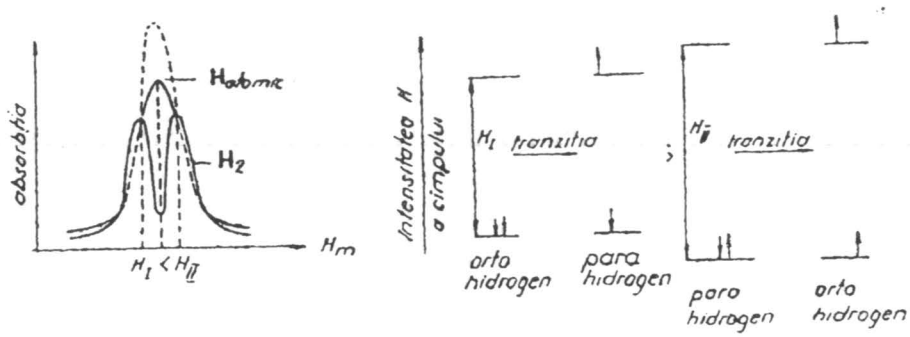

Figure 8. Fine structure of NMR spectrum of H_2 molecule

As a result of three distinct levels for the proton of the HD molecule results that the resonance sign is spitted into three components between which the middle one is twice higher. The curve of resonance:

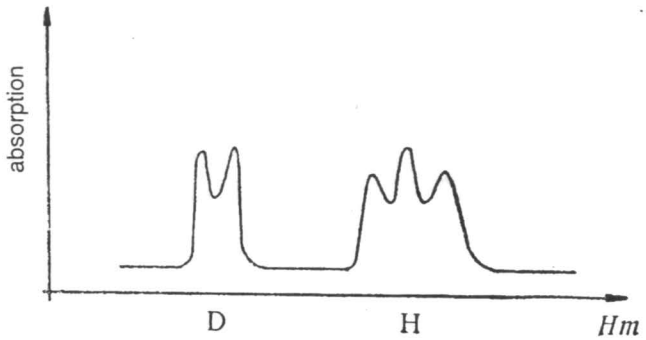

Figure 9. NMR spectrum of the HD molecule

Generally the moment multiplicity of nuclear magnetic moment 2I+1 is showed in the resonance curve by the fine structure with the same number of distinct components.

The fine structure of the NMR spectrum for the triphosphat anion is similar with that of H D molecule, with the difference that the ratios of the absorption intensities remain 2:1.

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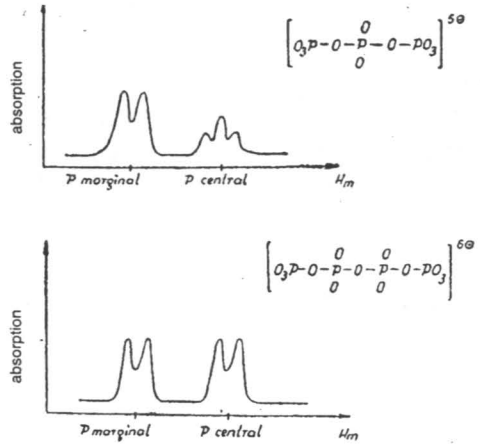

Figure 10. The fine structure of the NMR spectrum for $^{31}_{15}P$ of triphosphat and tetraphosphat anion

The tetra phosphoric anions has a fine structure consisting by two doublets of equal intensities. From the fine structure of NMR spectra can be deduced some spatial forms of molecules.

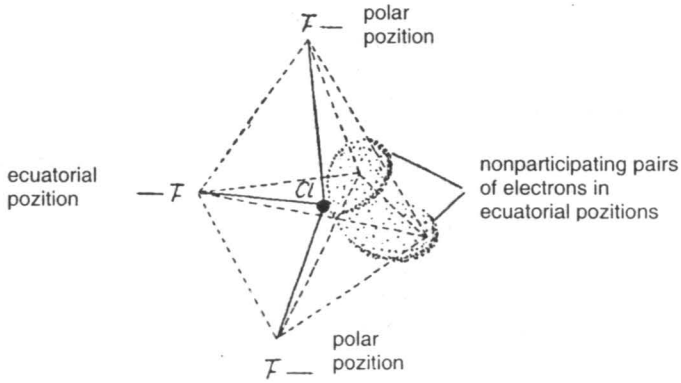

Figure 11. ClF_3 molecule structure

For example, if in the CF_3 molecule all F atoms would be equivalent from the point of view of the bonding electronic cloud of environment should appear only one signal of resonance in NMR spectrum.

In reality the resonance curve of the CF_3 consists by two maximums one, with a doublet and the other with a triplet of half intensity.

The NMR spectrum of ClF_3 confirms that two from the F ons are equivalent and the third has a different state in the molecule. To this one, corresponds the triplet signal. Into another example, SF_4 the atoms of the molecule should be placed in space like this:

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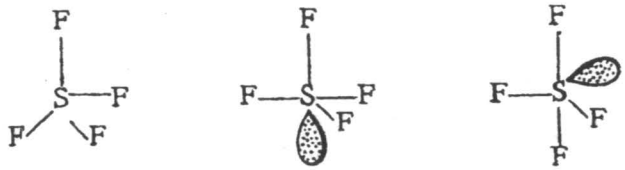

I II III

In the I arrangement the F ions being equivalent would have only one resonance signal, that would split into a fine structure of one quadruplet with the multiplicity 2I+1=4. The II arrangement implies two signals with the fine structure consisting in a doublet and a quadruplet in rapport with the intensity of 3:1.In the III arrangement the fine structure would consist of two signals, triplets of equal intensity produced by the same number of 2 atoms of F in both positions.

Experimentally in the NMR ${}^{19}_{9}F$ two signals are registered triplets of equal intensity fact that confirms that the real structure is the III[rd].

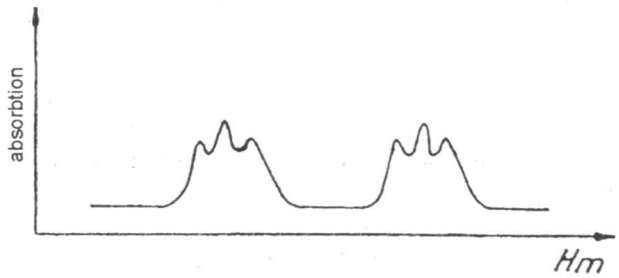

Figure 12. The NMR ${}^{19}_{9}F$ spectrum of SF_4

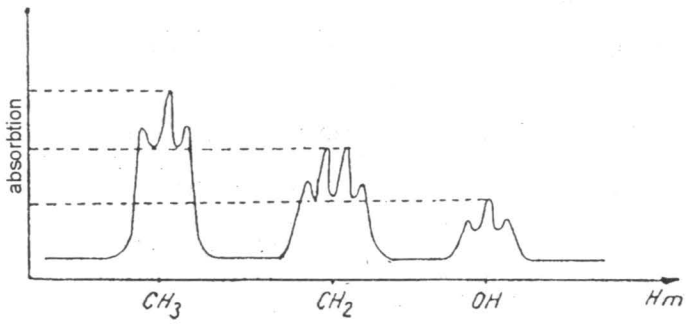

Figure 13. The NMR ${}^{1}_{1}H$ spectrum of ethanol.

The fine structure of the NMR ${}^{1}_{1}H$ spectrum of the ethanol is showed in the upper figure.

The H from CH_4 and OH give triplets because of the multiplicity 2I+1=3 from the group Ch_2 the methylene is signaled by a quadruplet under the influence of the 3H from CH_3. The quadruplet appears because of the multiplicity 2I+1=4 that comes from the spin orientations as we see below:

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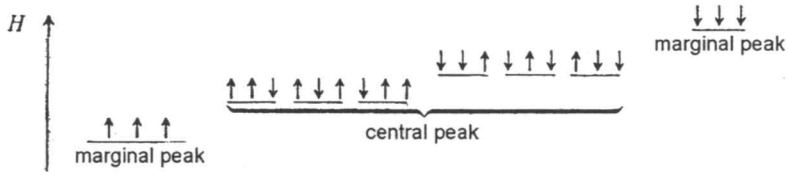

The fine structure of the CH_2 group should be influenced by H from the OH to, beside CH_3, but is not happening because of the vibrations of the proton from OH.

Electronic spin resonance ESR

We studied until now, about the magnetic effects of the nuclear fields and their interference with the magnetic field of the electronic shell from the atoms and with the other exterior fields. These interactions of these effects are at the base of some very important methods for finding some structure details of the substance.

The magnetic effect generated by electrons with non-compensed spin, from the atomic shell serves too at the knowledge of chemical substances. On this effect is based the research method like NMR called of electronic spin resonance.

The spin electronic magnetic field having ~2 10^3 times larger than the nuclear magnetic field Hm of order 10^4 gauss the frequency phenomenon is of ~2 10^3 times larger than the nucleus magnetic resonance. The absorbed energy for the ESR belongs to the frequency domain of the microwaves from electromagnetic spectrum.

Even if the ESR is the same NMR phenomenon it has to have an experimental tehnics much different because of the frequency of the used radius.

The information that can be obtained from ESR regards the molecules and ions that contain lone electrons. The fine structure of ESR spectra serves to determine the nuclear magnetism.

NUCLEAR REACTIONS

The nuclear reaction is a process that leads to charge in the atomic nuclei. They are of many types, after the nature of the particles of their energy and after the target-nuclide or after the resulting products.

1. Nuclear reaction produced by α particles

This kind of reactions showed the way for the obtention of some elements through nuclear systems.

The first reaction made used these particles for Bi of 5.5 MeV energy to scatter the gaseous N or the air passing through it. After the bombardment a proton was eliminated:

$$^{14}_{7}N+^{4}_{2}He=^{1}_{1}H+^{17}_{8}O \text{ or } ^{14}_{7}N(\alpha, p)^{17}_{8}O$$

The nuclear reaction that we study of (α, p) type implies a supplementary mass and energy , and it is called endoenergyc reaction:

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Examples:

$$^{10}_{5}B(\alpha, p)^{13}_{6}C$$

$$^{23}_{11}Na(\alpha, p)^{26}_{12}Mg$$

The discovery of the Neutron

At the bombarding of the Be with α particles from ^{210}Po it was observed that some radiations result without charge. They were called neutrons.

Nuclear Reactions with Accelerated Protons

The first reaction with protons was realized with H rays produced into a linear acceleration. By accelerating the protons until they reach 1.25 10^5 eV they can start a nuclear reaction like:

$$^{7}_{3}Li+^{1}_{1}H = 2^{4}_{2}He$$

For a nuclear reaction to be started with α particles they are accelerated by energies. There are known reactions of (p, α) like:

$$^{14}_{7}(p,\alpha)^{11}_{6}C=^{11}_{5}B$$
$$^{19}_{9}F(p,\alpha)^{16}_{8}O$$

or reactions with elimination of protons (p,n) type:

$$^{55}_{25}Mn(p,n)^{55}_{26}Fe=^{55}_{25}Mn$$

There are also nuclear reactions where the proton is added to the target nucleus, by (p,γ):

$$^{12}_{6}C(p,\gamma)^{13}_{7}N=^{13}_{6}C$$

Nuclear reactions produced with Deuterons

Like the proton, the deuteron of required energy can start a big number of reactions of different types:

1.(d,p)type:

$$^{2}_{1}H(d, p)^{3}_{1}H=^{3}_{2}He$$

2. Of (d, n) type:

$$^{2}_{1}H(d,n)^{3}_{2}He$$

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3. Of (d, α) type:

$$^{20}_{10}Ne(d,\alpha)^{18}_{9}F=^{18}_{8}O$$

In the case of feeble nuclei they can be considered fission r

$$^{6}_{3}Li(d\alpha)^{4}_{2}He(2\alpha).$$

Stellar Energy. Cosmo chemistry

The energy radiated by the Sun cannot be explained through the chemical reactions. By knowing the thermonuclear reactions it was possible the interpretation of the origin of the solar energy.

The most simple reaction possible on the Sun regards the fission of two protons:

$$^{1}_{1}H+^{1}_{1}H=^{2}_{1}H+^{0}_{1}e+\nu$$

And te fussion of two neutrons:

$$^{2}_{1}H+^{2}_{1}H=^{4}_{2}H$$

In the center of the Sun could take place other reactions like the C-N cycle. The reaction is: $4H^{+}=^{4}_{2}H+2e^{-}+2\nu$

The nuclei of C, N, O, are catalysts of the fission cosmochemistry that studies the formation of chemical elements and of other elements and compounds from the Universe.

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PERIODIC TABLE

In building up the periodic table by starting with the hydrogen atom and successively adding a proton to the nucleus and an electron on the extranuclear shell is called the Aufbau principle.

In multinuclear atoms, there are many complex forces:

- the attraction between the nucleus – electrons
- the repulsion among electrons
- the magnetic interaction.

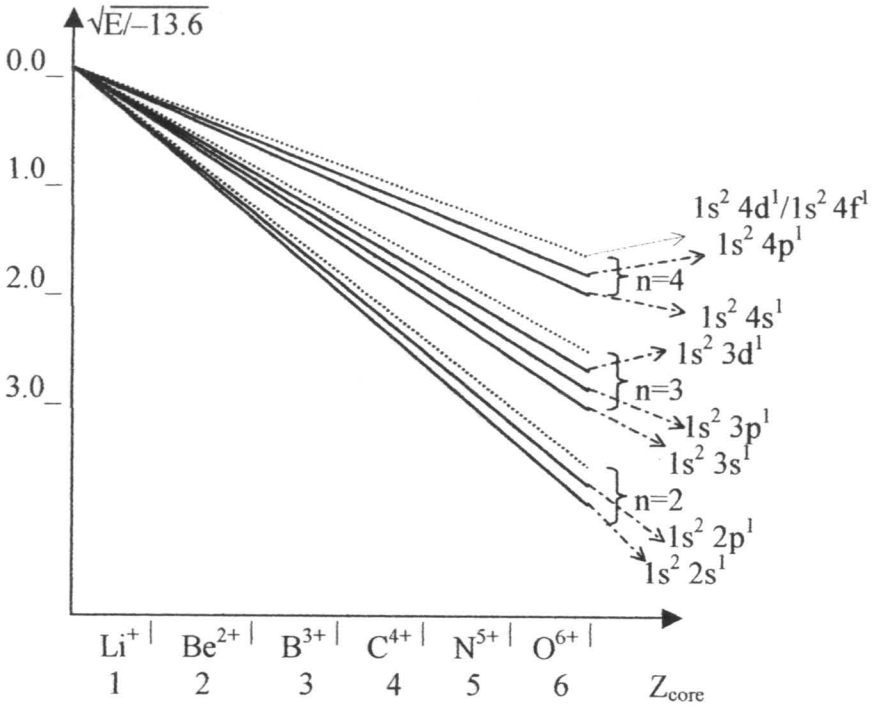
We must consider the moving of the electrons in an effective nuclear potential and the fact that electron – electron repulsion arises when more than one electron is present in an atom.

According to the equation derived for the Hydrogen atom:

$$E = -13.6\frac{(Z^*)^2}{n^2} \quad \text{where} \quad \frac{Z^*}{n} = \sqrt{\frac{E}{-13.6}}$$

$$Z^* = Z - \sigma \quad (\sigma - \text{screening constant})$$

Are described the Mosely diagram where dashed lines indicate the variation in the ion energy when $1s^2$ electrons completely neutralize +2 (two units of positive nuclear charge) and $Z^* = Z - 2$:



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The interesting feature is that the solid lines for the experimental ion energies are displaced from the theoretical lines by an amount that depends on the principal quantum number of the electron.

The deviation being largest for the $1s^2\ 2s^1$ configuration and decreasing for higher ion energy $1s^2\ nd^1$, $1s^2\ nf^1$ configurations is in agreement perfectly with the screening concept.

The 2s electron experiences a nuclear charge that is greater than (Z–2). In the other words the electrons do an incomplete job of screening nuclear charge. In $1s^2\ 2p^1$ configuration $1s^2$ electrons do a better job.

In each cases, the screening property of the $1s^2$ pair is least for ns and greatest for nd, nf configurations.

In this case, we can say that orbitals of the same n quantum number but different l quantum number may have different energies in a given atom. Starting from the Mosely relation, we may deduce the following empirical rule concerning the order of filling atom orbitals:

(a) orbital energies increase as (n+l) increases;

(b) for two orbitals with the same (n+l), the one with the smaller n lies lowest in energy.

Thus the order of filling becomes:

	1s,	2s,	2p, 3s,	3p, 4s,	3d, 4p, 5s,	...
(n+l)	1	2	3	4	5	

The combination of the quantum numbers underlines all interactions and determine the order of the energy levels. There are the following rules:

(i) *Pauli's principle:* in an atom there are not two electrons with the same quantum numbers (the same energetic state).

$n = 1, \ldots, +\infty$
$0 \leq l \leq n - 1;$
$m_l = 2l + 1$ values $(-l, \ldots, 0, \ldots, +l)$
$S = ½$
$m_S = 2S + 1$ values: $\pm 1/2, 0.$

If we consider the filling of orbitals only in this manner than the heaviest atom Z = 105 would build its configuration only with the first five levels.

Experimental data show that in the heavy atoms there are e^- on the orbitals with n = 6 or n = 7 and probably is another rule.

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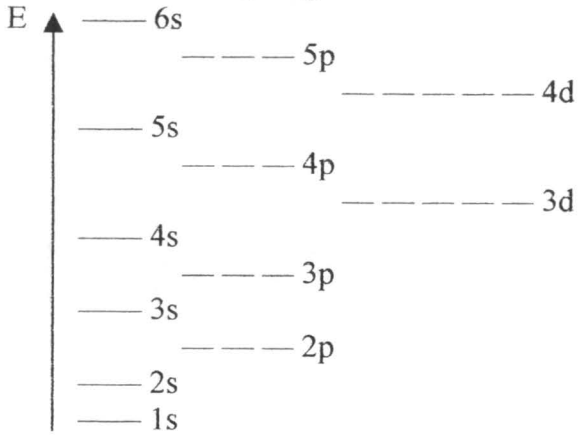
The shells (n)		The subshells (l)		The orbitals $\sum m_l = n^2$	The vacant places $2n^2$
K	n = 1	l = 0 (s)	1s □	$1^2 = 1$	$2 \cdot 1^2 = 2$
L	n = 2	l = 0 (s)	1s □	$2^2 = 4$: 1s	$2 \cdot 2^2 = 8$
		l = 1 (p)	3p □□□	3p	
M	n = 3	l = 0 (s)		$3^2 = 9$: 1s	$2 \cdot 3^2 = 18$
		l = 1 (p)		3p	
		l = 2 (d)		5d	
N	n = 4	l = 0 (s)		$4^2 = 16$: 1s	$2 \cdot 4^2 = 32$
		l = 1 (p)		3p	
		l = 2 (d)		5d	
		l = 3 (f)		7f	
O	n = 5	l = 0 (s)		$5^2 = 25$: 1s	$2 \cdot 5^2 = 50$
		l = 1 (p)		3p	
		l = 2 (d)		5d	
		l = 3 (f)		7f	
		l = 4 (h)		9h	

(ii) the sum (n + l) maximum and n = minimum

1s	2s	2p	3s	3p	3d	4s
n = 1	n = 2	n = 2	n = 3	n = 3	n = 3	n = 4
l = 0	l = 0	l = 1	l = 0	l = 1	l = 2	l = 0
1	2	3	3	4	5	4

It results the following diagram:



$1s^2$	$2s^2\ 2p^6$	$3s^2\ 3p^6$	$4s^2\ 3d^{10}\ 4p^6$	$5s^2\ 4d^{10}\ 5p^6$	$6s^2\ 4f^{14}\ 5d^{10}\ 6p^6$	...
2	10	18	36	54	86	105

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(iii) Charge correlation (e^2/r). Hund's rule.

Two particles with the same spin do a better job of avoiding each other in space than do two electrons of opposite spin quantum number. It is the spin quantum effect and it is observed for any particles that posses a spin angular momentum.

The physical significance is the repulsion energy between:

$E_{\downarrow\uparrow} - E_{\uparrow\uparrow} = \Delta E_{ex}$ $E_{\downarrow\uparrow}$ = the energy of electrons with different spin

$E_{\uparrow\uparrow} < E_{\downarrow\uparrow}$ $E_{\uparrow\uparrow}$ = the energy of electrons with the same spin

is less by an amount called "the exchange energy".

This principle is often named half – filled shell or Hund's principle.

Charge correlation dictates (e^2/r) that a lower energy situation exists if the two p electrons have different angular functions. Spin correlation further affords a lower (more negative) energy for spins alike.

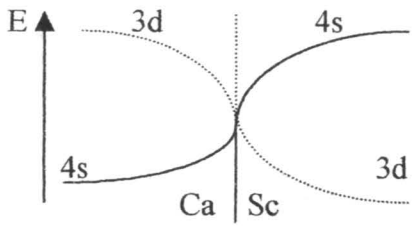
A good illustration can be found in the trends in ionization potential and electron affinity for the main groups from III to VIII (electron affinity is defined as the energy for the process $atom^- \rightarrow atom + e^-$). The valance configuration for these terms is $ns^2\ np^x$ where x progresses from 1 to 6. The increase of ionization potential and electron affinity (I and E) across the series is broken at $s^2\ p^4$ configuration. After this configuration the later series is simply shifted to lower potential.

For x = 1, 2, 3, the trend in ionization potential is determined by a balance between regularly increasing nuclear charge and regularly increasing electron repulsion.

For $s^2\ p^4$ configuration the last electron doesn't benefit from the "exchange energy" stabilization possible for the preceding three members of the series and further suffers from a large Coulombian repulsion.

Another illustration of the break down of the screening concept arises for the transition elements.

The orbital energy established from shielding effects accounts for the fact that 4s is filled prior to 3d on passing from Ca to Sc.



Z = 20 Z = 21

[Ar] $4s^2\ 3d^0$ [Ar] $3d^1\ 4s^2$

With scandium begins the first 3d series of transitional metals, where there are the so-called anomalies.

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$4s^2\ 3d^1$	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
			$3d^5\ 4s^1$					d^{10}	
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
		$4d^4$	$4d^5\ 5s^1$		d^7	d^8	d^{10}	d^{10}	
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
							$5d^9$	d^{10}	

Thus while the stability of "half filled shells" seems to be very good for Cr and Cu, fails for N.

The shielding concept was capable of accounting for the more stable 4s than 3d orbitals of K. This is the effect of the potential energy and the relative penetration of the radial part of 3d orbitals.

While the electron configurations of the transition elements in the zero oxidation state are difficult to interpret, the configurations of the divalent and trivalent ions are much simpler because they have $ns^2\ np^6\ nd^n\ (n + 1)s^0$ configuration and the orbital energy concept is reinstalled.

Another aspect regarding the outer shell:

K $1s^2\ 2s^2\ 3p^6\ 3s^2\ 3p^6\ 4s^1$

but: I_I of K $<$ I_I of Cu.

Cu $1s^2\ 2s^2\ 3p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

Why?

At the heavy elements the radial part of the orbitals on the outer shell penetrates the core of the atom and this phenomenon has as a consequence the contraction of the atomic volume. The greater will be the contraction, the greater will be the penetration of the orbital function.

V.1. **The Base of the Periodic Table**

Is considered to be the electron energy.

The energy of the electron within an atom is characterized up to now by the quantum numbers. These numbers correspond to the energetically shells and their values give an order to them.

The behavior of the electrons on an orbit is characterized by the principal quantum number n first for all introduced by Bohr and after 20 years it correspond to the shell filled with electrons.

For a given n, there is a set of quantum numbers.

n: principal quantum number (0,…,7)

quantise — the total energy on a shell

— the (total) speed of the electrons

l: secondary quantum number $l = n - 1$

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quantise — the angular kinetic momentum for a families of orbits (circular and elliptical)
— different values for l mean different energy of the subshells within a given shell (n)

l =	0	1	2	3
subshells	S	P	D	F
	sharp	principal	diffuse	fundamental

Are the initials used by spestroscopists in 1890 for the description of the spectral series of the alkali metals.

$m_l = 2l + 1$ values. $m_l \square [-l, 0, +l]$
quantise — the projection of the angular kinetic momentum on the main direction of a magnetic field (internal or external)
(it is the magnetic quantum number for the orbital motion of the electron).

$S = 1/2$ (is the spin quantum number)
quantise — the spin kinetic momentum
— the values corresponding to the particles called fermions

$m_S = 2S + 1$ values. $m_S \square [-S, 0, +S]$
quantise — the position of the spin kinetic momentum on the main direction of a magnetic field

Polyelectronic atoms. Multiplicity.

In 1929, Russell and Saunders discovered that the speed of an electron could combine to give a total speed.

B $1s^2\ 2s^2\ 3p^1$ — the magnetic properties are given by $2p^1$ electron and this atom behaves like an atom with one electron.

They suggested that there is a possibility of a vectorial combination between the angular kinetic momentum and the spin kinetic momentum of paired electrons and unpaired electrons and, for the valance shell, we can talk about a total angular momentum and a total spin momentum.

The vectorial coupling means a vectorial combination between the angular momentum of each electron and a vectorial combination for spin kinetic momentum for each electron.

$\sum \vec{L_\varphi} = \sum \vec{l_I}$; $\sum \vec{P_s} = \sum \vec{s_I}$.

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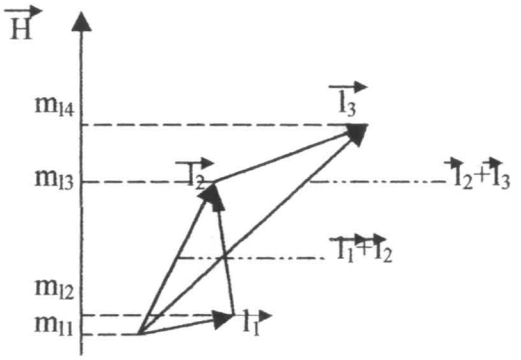

$\vec{L}_{total} = \vec{l}_1 + \vec{l}_2 + \vec{l}_3$

$\vec{L}_{total} = \sum m_{li}$

$\vec{P}_{s\,total} = \vec{s}_1 + \vec{s}_2 + \vec{s}_3 + \ldots$

$\vec{P}_{s\,total} = \vec{S} = \sum m_{si}$

2S + 1 = multiplicity

= the number of waves in the orientation of spin momentum regarding the main direction of a magnetic field on the main direction of the total angular kinetic momentum.

Monoelectronic atom					Polyelectronic atom				
l =	0	1	2	3	L =	0	1	2	3
subshell	s	p	d	f	microstates	S	P	D	F

In the case of polyelectronic atom we can not speak about a well defined ns, np or (n–1)d orbitals, but about a ground term given by the unpaired electron from the valance shell. This ground term can be denoted by T:

$$^{2S+1}T_J$$

where: 2S+1 is the multiplicity,

J – quantum number.

$$J = |L+S|, |L+S-1|, \ldots, |L-S|.$$

There are two kinds of vectorial coupling of the angular quantum number and the spin quantum number:

(i) LS coupling

–angular quantum number of each electron:

$\vec{L} = \vec{l}_1 + \vec{l}_2 + \ldots + \vec{l}_{\ldots}$

–and separately, the spin quantum number of each electron:

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$$\vec{S} = \vec{s_1} + \vec{s_2} + \ldots + \vec{s_n}$$

$$\vec{L} + \vec{S} = \vec{J}$$

where: J = the total angular moment of the atom

This kind of coupling gives very good results in explanation of the spectroscopic behavior of light atoms: $Z \leq 21$.

(ii) JJ coupling

–is computed the interaction between the angular and spin moments for each electron:

$$\vec{l_1} + \vec{s_1} = \vec{j_1}$$

$$\vec{l_2} + \vec{s_2} = \vec{j_2}$$

.....

$$\vec{l_n} + \vec{s_n} = \vec{j_n}$$

It results that the total angular moment of the atom is:

$$\vec{J} = \vec{j_1} + \vec{j_2} + \ldots + \vec{j_n}.$$

This coupling is used for heavier atoms.

To determine the shape of the final orbital (resulted after the coupling of the two moments) of the atom in the fundamental state or the possible orbits for the exited states, the following method is used:

–determine the L quantum number (in order to determine the microstate of the system):

$L = |\sum m_{li}|$

For example: np^3

$m_{l1}\ m_{l2}\ m_{l3}$

$L = 1\ (-1) + 1\ (0) + 1\ (+1) = 0 \Rightarrow {}^{2S+1}S_J$

–determine the total spin number:

$S = |\sum m_{si}|$

$m_{s1} = ½$

$m_{s2} = ½$

$m_{s3} = ½$

$S = 3 \cdot ½ = 3/2.$

From the total spin quantum number, find the multiplicity:

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$2S + 1 =$ multiplicity
$2S + 1 = 4$

–determine the total quantum number J:
$J = |L+S|, |L+S-1|, \ldots, |L-S|$.

In order to write the configuration, some rules can be applied:
- for the terms of the atom, the ground state is the state with the maximum multiplicity (S_{max});
- for more terms with the same multiplicity, the lower in energy term (the ground term) is the term with the secondary quantum number maximum (same S, maximum L);
- for terms with the same L, the lower in energy term is the following:
  - in the case of an orbital before half filled: the J for the ground state is given by $J = |L - S|$.
  - in the case of an orbital after half filled: $J = |L + S|$

example: $np^2 : J_{min} = |L - S|$
$np^4 : J_{max} = |L + S|$
for $np^3 : J_{min} = J_{max} = |L \pm S|$

For the example given above: $J = |L \pm S| = |0 \pm 3/2| = 3/2. \Rightarrow {}^4S_{3/2}$
To find the total microstates for each term:

$(2L + 1)(2S + 1) = 2J + 1.$ $(2\cdot 0 + 1)(2\cdot 3/2 + 1) = 2\cdot 3/2 + 1 = 4$ terms.

Using the rules:
a) the energy of an electron increases when n increases
b) the energy on an electron increases when (n + l) increases (this rule was explained on the basis of the penetration of R(r))
c) Pauli principle for exchange energy and charge correlation
d) Pauli exclusion principle observed first of all for fermions that can not have the same quantum numbers. Because the electrons are comparable with fermions, Pauli said that two electrons could fill the same orbital if they have opposite spins.

We can formulate the Periodic Table.

The order of filling the atomic orbitals is given by the penetration of some orbitals:

1s 2s 2p 3s 3p 4s 3d 2p 5s 4d 4f 5p 6s 4f 5d 6p 7s 5f 6d 7p

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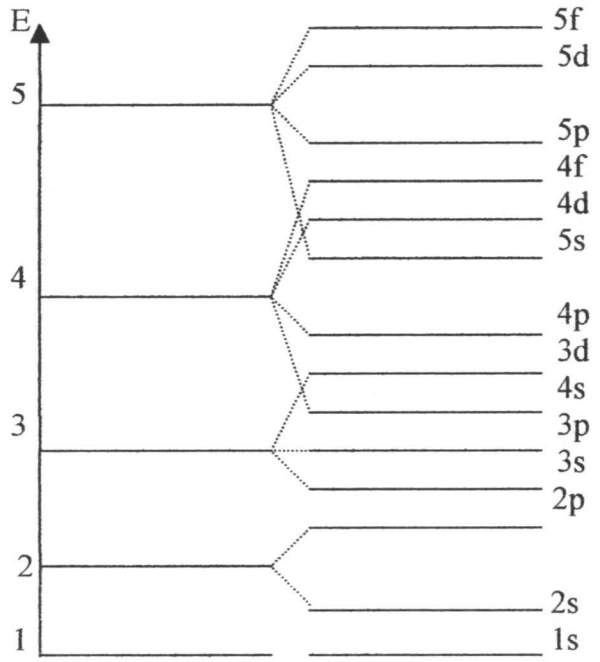

The name of the Periodic Table came from the periodicity of the properties of the elements observed first of all by The German chemist J. W. Döbereiner (1780–1849) who observed the relationship between (Ca, Sr, Ba) (Cl, Br, I) (Li, Na, K).

Chancourtois arranged the elements with increasing the atomic weight and obtained an elicoidal curve.

Dimitri Mendeleef (1834–1907) done the important step in 1871 and established the dependence of the atomic weight by physical and chemical properties very important in this being the valance. In the same time with Mendeleef, Lothar Meyer worked at the table. Both proposed a table with 8 columns (groups). The periodicity laws have immediately been accepted due to Mendeleef's success in prediction the unknown properties of the elements of a group.

The Periodic Classification of the Elements

If there are written the elements' symbols in the order of their increasing atomic numbers, it is observed the fact that the third element (lithium) has similar properties with the eleventh element (sodium), the fourth element (beryllium) with the twelfth (magnesium), etc. If, by neglecting the first two elements, hydrogen and helium, the sequence is interrupted after the tenth element (neon) and there are written, one under the other, the element symbols with similar properties, it is reached the next table (of the first 18 elements):

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Period 1							H	He
							1	2
Period 2	Li	Be	B	C	N	O	F	Ne
	3	4	5	6	7	8	9	10
Period 3	Na	Mg	Al	Si	P	S	Cl	Ar
	11	12	13	14	15	16	17	18

Applying next this principle, the periodic table can be obtained. There are seven horizontal rows called periods. While the first period contains only two elements, the next two periods (called short periods) contain each eight elements, the periods 4 and 5 contain each 18 elements, and the period 6 contains 32 elements (the period 7 is incomplete).

The vertical columns of the table, called groups of elements, have elements with chemical properties (and some of the physical properties) in a great resemblance.

A brief characterization of the elements will be done next.

a. *Hydrogen*: Has the atomic number Z = 1; it occupies a special place between all the chemical elements from which it is different by his characteristic chemical properties. *Helium* can be set next to hydrogen or as being the first rare gas.

b. *The elements from the principal groups*: Are set in the eight vertical columns called principal groups or a groups, denoted with Ia, IIa,..., VIIIa (the last one is often called the zero group).

c. *The transitional metals*: Their number is 30 and are grouped in rows of 10, in the periods 4, 5 and 6. By consequence, there are 10 subgroups or b groups of each three elements each. These are introduced, in the table, between the a groups of the corresponding periods (the group IIIb follows the IIa and the sequence is followed by IVb, Vb,..., VIIIb, IXb, Xb, Ib and IIb after which it follows the IIIa group).

d. *Lantanides and actinides*: form two families of 14 elements each that are introduced in the Table as follows: the first after the element lantan (Z = 57) and the second after actinium (Z = 89). Unlike the other elements, the lantanides and the actinides do not show the same periodicity in chemical and physical properties, but resemble with lantan and actinium.

V.2. **The Periodic Properties**

A) Physical properties that obey the law of periodicity:
- A.1. ionization energy,
- A.2. electron affinity,
- A.3. electronegativity,
- A.4. atomic and ionic volumes (radii).

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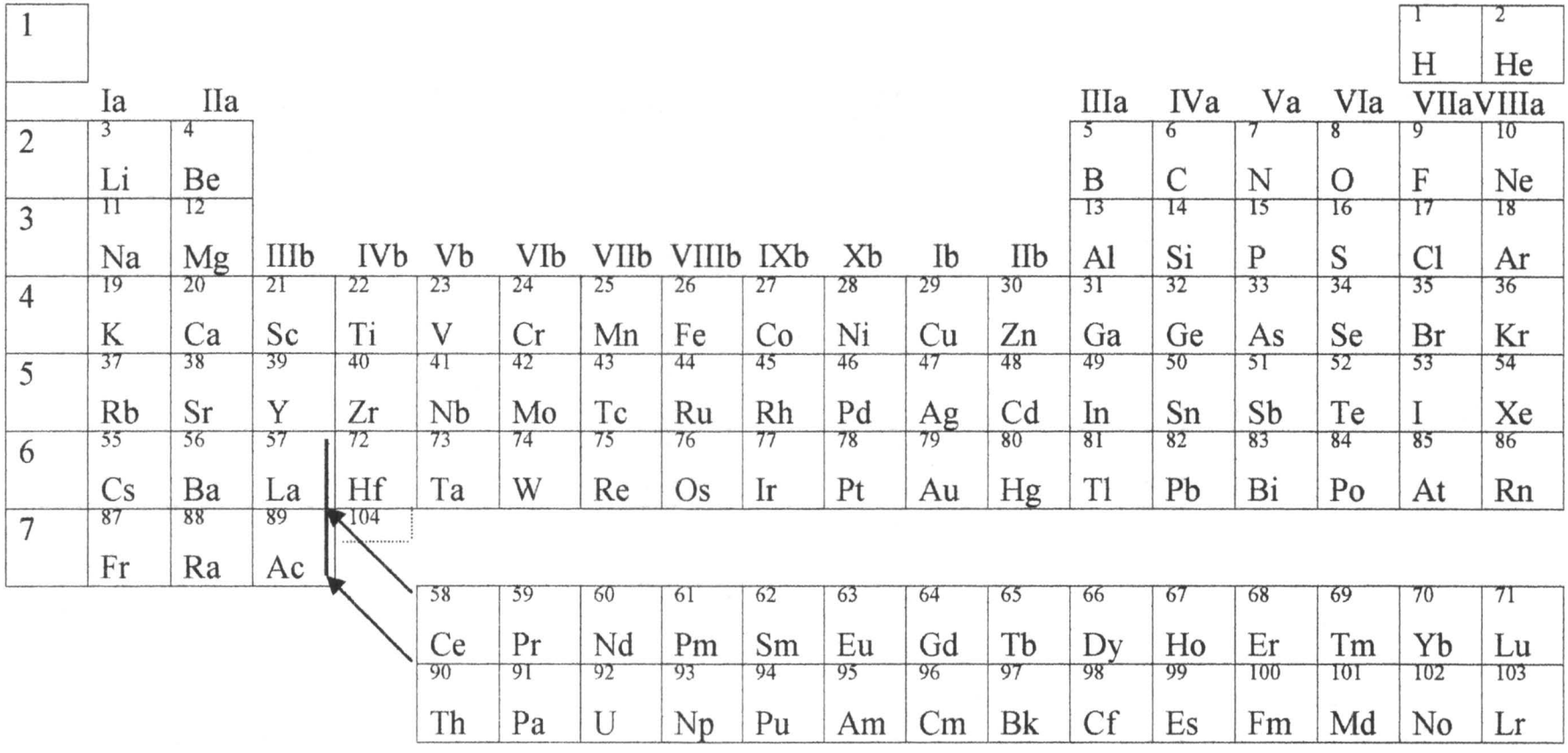

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B) Chemical periodic properties:
B.1. metallic character,
B.2. non-metallic character,
B.3. valance and oxidation states,
B.4. acid-basic character.

The most important part of the chemical theory is the law of periodicity. The properties of the chemical elements depend on the electronic structure of the atom and are variables of the atomic number in a systematic mod.

A. Physical Properties

A.1. *Ionization Energy*

$$Atom \rightarrow Atom^{+} + e^{-}$$

In general, the ionization energy increases on crossing a period (for example: Li through Ne) and decreases on descending a group (He through Rn).

These trends may be rationalized in terms of the electronic configurations of elements involved.

On crossing a period, the principal quantum number of the electron remains constant but the effective nuclear charge increases. In consequence, the electrostatic forces increase but not homogeneously. There are some discontinuities.

On descending on a given group, the principal quantum number increases (n) regularly and relatively more rapidly than the effective nuclear charge. Variations result primarily from changes in the type of orbital from which the electron is taken or from changes in the multiplicity of the ground state term.

- Elements with a ground state $^{1}S_{0}$ term have higher ionization energies than their neighboring elements (with some exceptions).

- This will be the ground state term for any element that has an outermost completely filled shell or subshell.

- The exceptions of this rule are the alkali-earth metals that have a transition metal as a neighbor. In this case the orbit of the s electron of the transition metal may be thought of in terms of the penetration of the d orbitals.

Hence, as the d electrons are filled in to build up the transition metals, the effective nuclear charge increases; in consequence, the ionization energy increases from alkali-earth metals through Zn.

In the case of Hg, not only the d orbitals but also the f orbitals have been filled in and the penetration effect in much larger. The ionization energy of Hg is almost as great as that of Rn.

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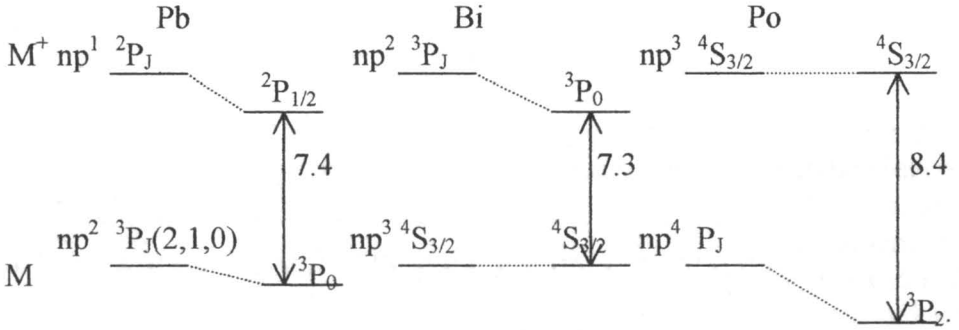
Following the Zn family elements, the ionization energy drops sharply for Ga, In, Tl, since the electron involved is a p electron that occupies a less penetrating orbit.

□ An interesting illustration of the importance of spin–orbit coupling is formed in the trend of ionization potential for the series:

	Pb	Bi	Po
	$6s^2\ 4f^{14}\ 5d^{10}\ 6p^2$	$6s^2\ 6p^3$	$6s^2\ 6p^4$
I:	7.4 eV	7.3 eV	8.4 eV

By definition, the value of the I for any atom is the difference in energy between the atom ground term and the ion ground term.



In the case of Bi, there is no spin coupling.
The energy of ionization:

$$E_I(I) = 13.60\ eV \frac{(Z-\sigma)^2}{n^2}$$

$$1eV = \frac{4.8 \cdot 10^{-10}}{300} = 1.602 \cdot 10^{-12}\ ergi = 1.602 \cdot 10^{-19}\ J = 3.801 \cdot 10^{-20} = 8.107 \cdot 10^3\ cm^{-1}$$

The higher ionization energy of nitrogen, as compared as those of its neighbors, may be attributed to the stabilizing influence of the spin–spin interaction, which are highest in filled and half–filled subshells.

Successive ionization energies increase in magnitude because of the smaller number of electrons left to shield the ionization electron from the nuclear charge.

Ahreus has pointed out that the oxidation states of the electrons in their compounds may be correlated by the difference in ionization energy for successive states, Δ_1 (I).

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If Δ_1 is around 10–11 eV or less, the lower state is not stable. Consider the experimental values for Al:

$$\Delta_{1,2} = 12.8 \text{ eV}$$
$$\Delta_{2,3} = 9.6 \text{ eV}$$
$$\Delta_{3,4} = 91.5 \text{ eV}$$

Theoretically:

$10\text{–}11 \geq \Delta_1 \geq 16$ $\quad M^+$ stable
$9.6 \geq \Delta_2$
$\Delta_3 \geq 50$ $\quad M^{3+}$ stable

Although compounds of Al (I) are stable as gaseous species, AlCl (g), they are unknown as solids. No compounds of Al (II) are known. Al (III) is the only stable state for Al compounds under usual conditions.

Δ_1 values of about 16 or above usually lead to stable states. Since Δ is always high at the noble gas configuration, these configurations frequently are formed for elements in their compounds.

The $s^2\ p^6\ d^{10}$ configuration is also one in which Δ is high and it is too a common configuration for positive ions.

The ionization energy for Li:

$$E_I^{Li} = E_{Li+}^{ion} - E_{Li}^{atom}$$

$$E_I = -13.6 \sum (Z^*/n^*)^2 \text{ eV}$$

$$E_I^{Li} = -13.6 \left[2 \left(\frac{Z^*}{n^*} \right)^2 1s^2 - \left[2 \left(\frac{Z^*}{n^*} \right)^2 1s^2 + 1 \left(\frac{Z^*}{n^*} \right)^2 2s^1 \right]_{atom} \right]$$

$$E_I^{Li} = 13.6 \cdot 1 \left(\frac{Z^*}{n^*} \right)^2 2s^1$$

$E_I = 13.6 \cdot 1 \cdot (1.30/2)^2 = 5.8$ eV – theoretically
5.4 eV – experimentally

A.2. *Electron Affinities*

The electron affinity of an atom is the energy involved in adding an electron to a gaseous atom in its ground state, to form a gaseous anion:

$$X_{(g)} + e^- \rightarrow X^-_{(g)}$$

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Sometimes the electron affinity is expressed the same as the ionization energy of $X^-_{(g)}$.

The electron affinity is expressed as a positive number (the amount of energy released). The factors affecting the electron affinity are the same as those affecting the ionization energy.

The trend within a group is less irregular than for ionization energies, but we must remember that the increase in size would cause the decrease in attracting an electron, whereas the increase in nuclear charge would cause the increase of attraction.

For the alkali metals, the size effect is more important and the electron affinities decrease from Li to Cs. This is also the general trend for most of the nonmetals with some considerable exceptions:

- The electron affinities of N, O and F are much lower than expected from the group trends, which are regular from S to Po and Cl to At. The ionization energies are regular within each of these groups and higher for N, O and F.
- Crossing a period the sizes decrease and the nuclear charges increase but while N, O, F have very high ionization energies, an addition of another electron is not so favorable as for P, S and Cl respectively.
- The factors causing low electron affinities for N, O and F lead to unusually low bond energies when these elements are bonded to themselves or to one another by single bonds.
- The noble gases have stable ns^2 np^6 configurations ($1s^2$ for He) and the affinity is approximately zero or slightly negative (corresponding to endothermic processes) indicates that there is no bound state for the added electron.
- The configurations $(n-1)d^{10}$ ns^2 have a negative affinity.
- The state (^2P) is too high in energy for the favorable addition of an electron.
- The affinities are very high for the neighboring elements Pt and Au.

Affinities:

H	O	F
16.5	~30	83
	S	Cl
	~40	86.5
		Br
		81.5
		I
		74.2

A.3. *Electronegativity*

Electronegativity has already been used in the discussion of oxidation numbers, formal charges, in resonance structures and can be defined as the attraction of the electrons involved in a chemical bond by one of the atoms.

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Within a periodic family the electronegative character generally decreases with increasing atomic radius, although there are some exceptions.

(a) Pauling's Electronegativity scale

Pauling established a scale of electronegativity based on "excess" bond energies. The energy of a bond D(A–B) is a sum of nonpolar contribution, Dnp(A–B), and a polar contribution Dp(A–B):

$$D(A–B) = Dnp(A–B) + Dp(A–B)$$

Dnp(A–B) is expected from the meaning of the nonpolar energies:

$$Dnp(A–B) = \frac{D(A–A) + D(B–B)}{2}$$

Δ is a measure of the bond's expected polarity which results from a displacement of the electronic charge towards an atom.

$$\Delta = D(A–B) + \frac{D(A–A) + D(B–B)}{2}$$

Dnp'(A–B) experimentally determined is less than Dnp(A–B) theoretically computed. The difference between them is designated with Δ:

$$\Delta = Dnp'(A–B) – Dnp(A–B)$$
$$\Delta = Dnp'(A–B) – 1/2[D(A–A) + D(B–B)]$$

When $\Delta<0$ represents a molecule is the more stable in the ground state comparing with the other structures of it.

Pauling suggested the using of the electronegativity coefficients: χ computed from the heat of formation of the compound AB (ΔH_f):

$$(\chi_A – \chi_B) = 0.102 \sqrt{-\Delta H_f}$$

0.102 was computed taking a standard element $\chi_{Li} = 1$
and for a AB_n compound:

$$(\chi_A – \chi_B) = 0.102 \sqrt{-\frac{\Delta H_f}{N}}$$

$$-\Delta H_f = n \times 96.49 (\chi_A – \chi_B)^2 \text{ where:}$$

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– the difference $\chi_A - \chi_B$ is a measure of the distortion of the covalence between A–B.

The electronegativity of an atom has a constant value and depends on the nature of the bond, its oxidation state, the type of hybridization.

- The electronegativity increases when the oxidation state increases;
- The elecronegativity increases when the coordination number of the donor atom increases and it decreases when the coordination number of the acceptor atom increases.

Standard: $\chi_{Li} = 1$.

(b) Mulliken Method

One of the more important uses of the atomic terms energies have is the definition of the electronegativity.

The original ideas were advanced by Mulliken and more recently applied by Hinze and Jaffe.

Mulliken began with the definition of electronegativity by considering electron transfer between two atoms A and B:

$$A^-B^+ \leftrightarrow A^+B^-$$

If the electronegativities of A and B are identical, the two ionic pairs would have the same energy.

$E_{A^-B^+}$: depends on

the ionization energy of B: I_B: $B \rightarrow B^+ + e^-$ and

the electron affinity of A: E_A: $A^- \rightarrow A + e^- \Rightarrow -E_A$: $A + e^- \rightarrow A^-$

$$E^{(1)} = I_B - E_A$$

$E_{A^+B^-}$: depends on

the ionization energy of A: I_A: $A \rightarrow A^+ + e^-$ and

the electron affinity of B: E_B: $B^- \rightarrow B + e^- \Rightarrow -E_B$: $B + e^- \rightarrow B^-$

$$E^{(2)} = I_A - E_B$$

$$E^{(1)} = E^{(2)}$$

$$I_B - E_A = I_A - E_B$$

$$I_B + E_B = I_A + E_A$$

If A is more electronegative then B: $I_A + E_A > I_B + E_B$

In this situation, we must calculate the energy of the atom A in its ground state as an average of all terms, then the energy of A^+ and A^- as an average of all terms too.

Ground state energy:

$C\ (ns^2\ np^2)$ $\quad E = 1/15\ [\ 1 \cdot E(^1S) + 5 \cdot E(^1D) + 9 \cdot E(^3P)]$

$C^-\ (ns^2\ np^3)$ $\quad E = 1/20\ [\ 4 \cdot E(^4S) + 6 \cdot E(^2P) + 10 \cdot E(^2D)]$

$C^+\ (ns^2\ np^1)$ $\quad E = 1/6\ [\ 6 \cdot E(^2P_{1/2})]$

Thus the electronegativities are different for an orbital 2S and 2P, orbital electronegativities vary with the type of hybrid and the relative S and P character of the hybrid.

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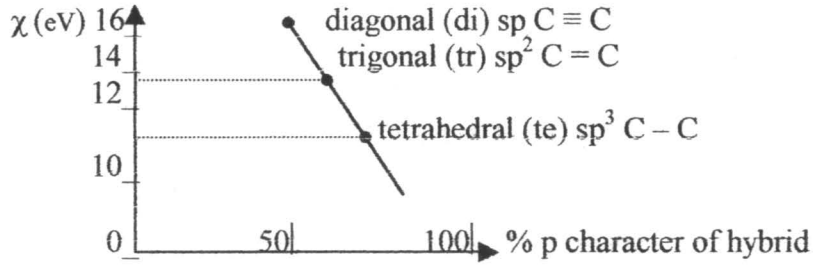


Historically, Pauling was the first to introduce the concept of electronegativity in terms of the derivation of the AB bond energy from the mean AA and BB bond energies.

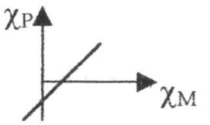
Since: D(A–B) > 1/2[D(A–A) + D(B–B)] – the bond energy is greater then the average, Pauling attributed this difference to contributions of ionic resonance forms to D(A–B) bond energy.

$$A - B \leftrightarrow A^+B^-$$

Mulliken electronegativities are generally (with some exceptions) linearly related to the Pauling values:

$$\chi_P = 0.34\,\chi_M - 0.2$$

where: $y = mx - n$



(c) Allred and Rochow

The electronegativities are related to Slater's rule.

They considered the force acting on a valance electron of an atom to be a good measure of the ability of the atom to attract electrons. This force is given by:

$$|F| = e^2 \frac{Z^*}{r^2}$$

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where r is the covalent radius of the atom: $r = r_{cov}$.

These forces are generally linearly related to the Pauling electronegativities of the atom χ_P:

$$\chi_P = 0.36 \frac{Z^*}{r_{cov}^2} + 0.7$$

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A.4. *Atomic and Ionic Radii*

The atomic radius can be determined by X–ray or electron diffraction. In any period there is a decrease in atomic radius from left to right. This is surprising because from sodium to chlorine there is an addition of six protons, six electrons and a number of neutrons and in spite of all these; the atomic radii fall from 0.157 nm to 0.099 nm. The explanation is that the extra electrons are being added to the same 3s and 3p orbitals (therefore there is no increase in size) but the extra nuclear charge attracts these electrons drawing them closer to the nucleus.

For the elements I a group of the Periodic Table, the atomic radii increase down in the group. Down in group, extra electrons are added to additional orbitals. Despite the extra nuclear charge and because of increased screening, there is a net increase in atomic radius down the group.

The trends in ionic radii are similar with those of the atomic radii.

A method to determine the ionic radii is based on the formula:

$$\frac{r_c}{r_a} = \frac{Z^*_c}{Z^*_a}$$

Experimentally, from the X–ray data: $r_c + r_a$ = number.

r_c – the radius of the cation,

r_a – the radius of the anion.

Example:

Na^+:	σ
$1s^2$	$2 \cdot 0.30 = 0.60$
$2s^2\ 2p^6$	$2 \cdot 0.85 + 7 \cdot 0.35 = 4.15$

$Z^*_{Na^+} = 11 - (0.60 + 4.15) = 6.25$

$Z^*_{F^-} = 9 - 4.75 = 4.25$

$r_{Na^+} / r_{F^-} = 6.25/4.25$ $\qquad$ $r_{Na^+} = 0.95$Å

$r_{Na^+} + r_{F^-} = 2.31$ Å $\qquad$ $r_{F^-} = 1.36$Å

Cations have a smaller radius than the corresponding atoms:

Na 0.157 nm $\qquad$ Na^+ 0.095 nm

The removal of one electron from a sodium atom employs the 3s orbital. The outer electrons are therefore in a 2p orbital.

Anions have a larger radius than the corresponding atom because of repulsion between the electrons. There is no extra nuclear charge.

F 0.064 nm $\qquad$ F^- 0.136 nm

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Some ionic radii (in Å, after Pauling):

– ions with eight electrons in the exterior shell (rare gas configuration):

3–	2–	1–	1+	2+	3+	4+	5+	6+
		H	Li	Be	B			
		1.53	0.60	0.37	0.20			
N	O	F	Na	Mg	Al	Si		
1.71	1.40	1.36	0.96	0.65	0.50	0.41		
P	S	Cl	K	Ca	Se	Ti	V	Cr
2.12	1.84	1.81	1.33	0.99	0.81	0.68	0.59	0.52

– cations with eight electron shell:

1+	2+	3+	4+	5+
Cu	Zn	Ga	Ge	As
0.96	0.74	0.62	0.53	0.47
Ag	Cd	In	Sn	Sb
1.26	0.97	0.81	0.71	0.62
Au	Hg	Tl	Pb	Bi
1.37	1.10	0.95	0.84	0.74
		Tl^+	Pb^{2+}	
		1.44	1.21	

– other cations:

Ti^{3+}	V^{3+}	Cr^{3+}	Mn^{3+}	Fe^{3+}		
0.69	0.66	0.64	0.62	0.60		
			Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}
			0.80	0.75	0.72	0.69

Each of the horizontal row contain isoelectric ions (ions having the same number of electrons in the shell). In each horizontal row, the ionic rays decrease from left to right because of the increase of the nuclear charge. The electrons, equal in number, are more attracted to the nucleus as the charge increases.

When a metal can form different cations, the cation with bigger electrovalance has a smaller volume (less electrons that are strongly attracted to the nucleus because of its higher positive charge).

Ionic rays for the oxidation states +4, +5 and +6 correspond actually to covalent oxidation states.

These ionic radii correspond to a coordination number of 6 and a NaCl lattice.

Atomic rays can be determined from nonionized compounds in crystalline state and reflects the atom dimensions better then the atomic volumes. From the variation of the atomic rays versus atomic number it can be seen that the atomic rays of alkali metals and of monatomic gases Ne, Ar, Kr and Xe have highest values and the atomic rays of the d metals have smaller values.

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B. Chemical Properties

B.1. *Metallic Character*

In periods, the electropositive (metallic) character also called electropositivity, decreases from left to right. Because of this fact, the strong electropositive elements are placed on the left side of the Periodic Table. The atoms of strong electropositive elements give easily their valance electrons, being transformed in positive ions (cations).

Metallic ions have in their exterior shell the same number of electrons as the atoms of monatomic gas atoms before them in the Periodic Table. For instance, the ions of alkali metals have in these shell eight electrons, except the Lithium ion and the Helium atom that have two electrons.

Ions have a chemical stability higher then the one of the atoms from which they came from. For instance, the Sodium atom gives his valance electron from a 3s orbital, becoming the Na^+ and getting the octet configuration of Neon $1s^2\ 2s^2\ 2p^{6+}$. While the Sodium atom manifests an increased chemical reactivity, decomposing the water at the usual temperature:

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$

the Sodium ion is stable and doesn't decomposes the water but it gets hydrated with eight molecules of water: $Na^+ \cdot 8H_2O$.

In groups, the electropositivity (Ep) increases from up to down. For the group I A, the electropositivity increases from Li to Cs:

$$Ep_{Li} < Ep_{Na} < Ep_{K} < Ep_{Rb} < Ep_{Cs}.$$

In the case of the transitional metals, the electropositivity decreases from up to down. For instance: the electropositivity f copper is higher then the one of silver:

$$Ep_{Cu} > Ep_{Ag} > Ep_{Au}.$$

A similar relation can be obtained in the case of the Zinc family:

$$Ep_{Zn} > Ep_{Cd} > Ep_{Hg}.$$

In conclusion, the electropositivity of the transitional metals varieties inverse proportionally with the one of the metals from the main groups.

The reactivity of metals in compounds is as follows:

– In groups, the basicity of hydroxides increases from up to down in agreement with the increase in electropositivity. In periods, the basicity of hydroxides decreases from left to right according to the decrease of the electropositivity and the acidity of these hydroxides increases in the same time.

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B.2. *Nonmetallic Character*

In periods, the electronegative character (electronegativity), also called the nonmetallic character increases from left to right. Because of this fact, the most electronegative character is placed on the right hand of the Periodic Table.

The atoms of the strong electronegative elements accept easily electrons and become negative ions (anions).

In groups, the electronegativity decreases from up to down. For instance, the electronegativity (En) decreases in the group VII A as follows:

$$En_F > En_{Cl} > En_{Br} > En_I.$$

Fluorine is the most electronegative from all the halogens and all the nonmetals.

Nonmetallic ions have the tendency to form with hydrogen acidic compounds and the character is increasing, in periods, from left to right. So H_2S is a weak acid and HCl is a strong one.

The hardness of oxoacids increases in the same time as the nonmetallic character increases. The straight of oxoacids is also increasing with the increase of the oxidation state. The same is for nonoxidizing acids.

B.3. *Valance and Oxidation States*

It was first believed that the maximum valance of an element is equal to the group number of the element in the Periodic Table. Like it can be seen in the table below, this rule is not a general one. This can be applied for the oxides and fluorides of the principal groups, but not for the hydrides of this elements and not for the combination of the other nonmetals with the alkali and alkali–earth metals. As for the transitional metals, this rule is applied for the groups IIIb–VIIb, but not for Cu, Ag, Au (group Ib) that surpass, in some combinations, the number of the group (can be di– or trivalent). Also, this rule is applied only for the last two elements of the group VIIIb, Ruthenium and Osmium (RuO_4, OsO_4), that form the only binary combinations where one of the elements have the valance eight. There are no valances higher then eight in any binary combination. Many elements form binary combinations having valances higher then the number of the group.

In the table below are shown the formulas for the hydrides, oxides and fluorides of some elements (R is the element):

Group	I	II	III	IV	V	VI	VII	VIII
Hydrides	RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH	—
Oxides	R_2O	RO	R_2O_3	RO_2	R_2O_5	RO_3	R_2O_7	RO_4
Fluorides	RF	RF_2	RF_3	RF_4	RF_5	RF_6	RF_7	RF_6

On the base of oxidation state is the principle that:

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–fluorine and oxygen are, in their combination, electronegative and with the oxidation state –1 and –2, respectively (the exception being the compound hydrogen peroxide where the oxygen has the oxidation state –1: H_2O_2);
–the elements from the group Ia (alkali metals) – Li, Na, K, Rb, Cs – and the ones from the group IIa (alkali–earth metals) – Be, Mg, Ca, Sr, Ba, Ra – are, in all their combinations, electropositive and have the oxidation state +1 (group Ia elements) and +2 (group IIa elements).

So, the oxides with formulas:

I	II	III	IV	V	VI	VII
Na_2O	CaO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
			TiO_2	V_2O_5	CrO_3	Mn_2O_7

Are written as having the oxidation states:

$2Na^+ O^{2-}$ $Ca^{2+} O^{2-}$... $Si^{4+} 2O^{2-}$... $S^{6+} 3O^{2-}$ $2Cl^{7+} 7O^{2-}$

In this formulas, electric charges have a formal character and do not represent real ionic charges in all the cases (do represent for some cases as for Na_2O, CaO).

The sign minus or plus is attributed to an element in function of the electronegativity of the second element present in the combination. In combinations like $SiMg_2$, SNa_2 and ClNa, silicon, sulfur and chlorine have negative states; in combinations like SiF_4, SCl_2 and Cl_2O, these elements have positive oxidation states.

A rule can be formulated:

–in their combinations with more electronegative elements, the maximum oxidation states are positive and equal to the number of the group in the Periodic Table;

–in their combinations with more electropositive elements, the oxidation states are negative and equal with eight minus the group number.

–the sum of the positive and negative charges in a compound must be equal to zero.

The anomaly of valance of hydrides is explained by the fact that hydrogen is in one of its electronegative combinations H^-. Hydrogen has an electropositive state: H^+ (normal). Hydrides of period two elements:

LiH BeH_2 BH_3 CH_4 H_3N H_2O HF

Can be written as having the oxidation states:

$Li^+ H^-$ $Be^{2+} 2H^-$ $B^{3+} 3H^-$ $\{C^{4+} 4H^- \text{ or } C^{4-} 4H^+\}$ $3H^+ N^{3-}$ $2H^+ O^{2-}$ $H^+ F^-$

In the case of hydrides of groups I–IIIa and IVa, the elements oxidation states are equal with the number of the groups. For the groups Va, VIa and VIIa, the oxidation states are negative and equal to 8 – 5, 8 – 6 and 8 – 7. For group IVa

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elements, like carbon and silicon, the oxidation state can be formally considered as being positive or negative.

The oxidation state concept is meant to replace the valance concept.

B.4. *Acid – Basic Character*

In the case of acids, there are a few characteristics that are sketched:

–the strength of acids can be put in an increasing order of the electronegative character:

the acidity of oxoacids $H_3PO_4 < H_2SO_4 < HClO_4$.

By analogy with the metallic character, where the basic character of hydroxides was decreasing in a period from left to right, can be seen that the acidic character of these oxoacids is inverse:

$$PO(HO)_3 < SO_2(HO)_2 < ClO_3(HO)$$

The straight of these oxoacids is also increasing with the increase of the oxidation state:

$$HClO < HClO_2 < HClO_3 < HClO_4.$$

The acidity of nonoxidizing acids HF > HCl > HBr > HI.

— in groups, the basicity of hydroxides increases from up to down in agreement with the increase in electropositivity. For instance, in the second principal group: $Be(OH)_2$ is amphoter, $Mg(OH)_2$ is a weak base, $Ca(OH)_2$ has the usual reactivity of a base, $Sr(OH)_2$ is a hard base, but the hardest is $Ba(OH)_2$.

In periods, the basicity of hydroxides decreases from left to right according to the decrease of the electropositivity and the acidity of these hydroxides increases in the same time. For instance, NaOH is a strong base, $Mg(OH)_2$ is a weak base and $Al(OH)_3$ is amphoteric.

Chemical Properties and Electronic Structure of Atoms

All the chemical phenomena of atoms have as cause the exterior electronic shell modifications.

The tendency of atoms to combine is due to the unstability of their electronic configuration and the same observation is true for molecules.

The periodic variation of chemical properties of elements (valance, electrochemical character) and some of the physical properties (melting point, boiling point, atomic radii, thermal and electrical conductivity...) can be explained in function of the electrons number in the exterior shell of the electronic configuration.

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As a consequence, it is observed a came back of the chemical properties, from one period to another, for the elements of the same group. This is because the atoms of the same group have the same number of electrons in the valance shell (some exceptions are met for the transitional metals). These chemical properties are somewhat different from the qualitative point of view because of the different number of electronic subshells.

As for the valance, the maximum valance* of all the elements from the principal groups** of the Periodic Table, except oxygen, fluorine and the rare gases, is equal with the electron number in the exterior shell (valance electrons).

The atoms of elements in the secondary groups** have the valance electrons on two shells: on the exterior s shell and on the subshell d, so all these electrons can contribute to a valance. The maximum number of valance is corresponding to the number of the group; the last elements that can reach the maximum number of the group are the elements from the iron group: ruthenium and osmium, but not iron and this is VIII. The availability of the electrons of the d subshell is the reason for the fact that the transitional elements can display several valances different from the maximal one but smaller.

As for the electrochemical character, it is observed that, for the elements which have in the exterior shell few valance electrons (groups I, II, III A), the stable electronic configuration it is attained by the easy release of the valance electrons and, so positive ions are formed. These elements are electropositive. On the contraire, the elements of groups VI and VII A can develop easier the stable rare gas electronic configuration by accepting electrons and forming negative ions. These elements are electronegative.

In a period, the electropositive character of elements, meaning the easiness to release exterior electrons, decreases from left to right in the same way as the electronegative character is increasing, meaning the affinity for electrons. So, the variation of the electrochemical character of elements is depending on the electronic configuration, on the possibility to attain a more stable configuration (of the rare gas).

In regard to the Periodic Table, considering the electronic filling of shells, after the distinctive electron placement in one of the orbitals: s, p, d or f, the elements can be grouped in four categories:

1.elements from the principal groups I and II that have the distinctive electron in a *s* orbital;

2.elements from the principal groups III, IV, V, VI, VII and VIII that have the distinctive electron in a *p* orbital;

3.transitional elements from the secondary groups that have the distinctive electron in a *d* orbital;

4.lantanides and actinides that have the distinctive electron in an *f* orbital.

---

* The maximum valance of an element versus oxygen results by the release of the valance electrons and the maximum valance versus hydrogen results by accepting in the exterior electronic shell of electrons until the number eight is accomplished.

** In the old numbering of groups of the Periodic Table.

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V.3. **Relations inside the Periodic Table**

Like a general rule for the Periodic Table groups, the first element of group display different properties from the rest. For instance:

- In the group VII A, elemental fluorine is more reactive then the other halogens.

- In group VI A, oxygen is different in its elemental state and in it's combinations from the other elements of the group.

- In group V A are also important differences: the first element, nitrogen N (period 2) has different properties then phosphor P and arsenic As (periods 3 and 4). Those are also different from antimony Sb and bismuth Bi (periods 5 and 6) whose metallic character is very pronounced.

- In group IV A, carbon C (period 2) is very different from the rest. While carbon has a definite nonmetallic character, tin Sn and lead Pb are well defined metals and, in between, silicon Si and germanium Ge are semimetals and have semiconductor properties.

- In group III A, the elemental boron B resembles much silicon Si. The crystal of elemental boron, with an unusual and complicated structure, is made up of atoms connected by strong and by directed in space bonds. His explains unusual hardness and the high melting point that resembles those of carbon. The other group III elements, in the elemental state, have a metallic character.

- In group II A, beryllium Be differs from the other elements because, in its combinations forms covalent compounds, not ionic like the rest of the group.

- In group I A, lithium Li is the less electropositive and francium Fr is the most electropositive. Like the other groups of the Periodic Table, lithium differs from the point of view of properties and behavior from the other group elements. In many of its properties, lithium resembles magnesium, the second element of the next group (diagonal relationship).

Another diagonal relation is the one between beryllium and aluminum. For instance, Be hydroxide is different from the rest of elements from its group (and resemble Al hydroxide) by the fact that it dissolves in concentrated solutions of NaOH or KOH and give beryllates. Also the aluminum hydroxide forms, with alkali hydroxides, aluminates, soluble in water:

$$Al(OH)_3 + HO^- \rightarrow [Al(OH)_4]^- \quad \text{or}$$
$$Al(OH)_3 + 3\,HO^- \rightarrow [Al(OH)_6]^{3-} \quad \text{and}$$
$$Be(OH)_2 + 2\,HO^- \rightarrow [Be(OH)_4]^{2-}.$$

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THE CHEMICAL BOND

The chemical compounds contain joint atoms through chemical bond. Through chemical bond the atoms stabilized as cations or anions with a noble gas configuration (e.g. O^{2-}, Cl^{-}, N^{3-}, K^{+}, Mg^{2+}, Al^{3+}) or pseudo noble gas (e.g. Zn^{2+}, Cd^{2+}, Ga^{3+}).

The metals lose the outer shell electrons to form stable cations and the nonmetals require electrons to form anions. These processes are called ionic valence states and may be predicted from the electronic configurations. Another mode to stabilize the atoms in a chemical compound is to form covalent bond between the atoms. The unpaired electrons of the outer shell are shared and form a covalent bond. In this way each of atoms obey the octet rule.

THEORETICAL TREATMENT OF IONIC BOND

The Nature of the Ionic Substances

Most ionic compounds are formed by combination of elements near "opposite ends" of the periodic table. They are usually oxides, sulphides or halides of the electropositive metals such as those of groups I, II, III and the transition series. The main requirement for the formation of the ionic compounds, that is, those solids which consists of an array of positive and negative ions held together almost entirely by the coulomb forces between the oppositely charged ions, are the metal ions which have a relatively low ionization potential and that the nonmetals atoms or radicals have a relatively high electron affinity.

Lattice Energies of Ionic Crystals

As an example of an idealized ionic substance let us consider a 1:1 compound of the type $(M^{+})(X^{-})$. M^{+} is the cation, spherical in shape, incompressible and X^{-} is the spherical anion, also incompressible and having a definite size. This kind of model is commonly called a hard sphere electrostatic model. When these cations and anions are brought together in large and equal numbers, they will arrange themselves in a regular array in which they trend to occupy the minimum volume and have the least electrostatic energy. This arrangement adopted is that is shown in the Figure 1.and this type of lattice arrangement occurring in sodium chloride.

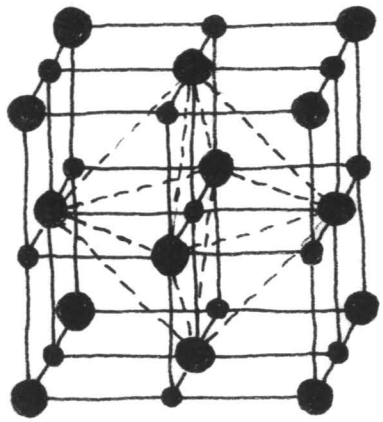

Figure 1. The sodium chloride structure

M-X is the distance r; using the Figure 1 and the simple trigonometry it can be shown that M^{+} ion is surrounded by six X^{-} ions (nearest neighbors) at a distance r, twelve ions (second nearest neighbors) at a distance $\sqrt{2}r$, eight more distant X^{-} ions at $\sqrt{3}r$, six M^{+} ions at 2r, twenty-four more ions at $\sqrt{5}r$ etc.

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The electrostatic interaction energy of the M^+ ion with each of these surrounding ions is equal to the product of the charge on each ion, Z_e^+ and Z_e^- ,divided by the distance. Hence the electrostatic energy can be written:

- six attraction at the distance r
- twelve repulsions at the distance $\sqrt{2}r$
- eight attractions at the distance $\sqrt{3}$ (corners)
- six attractions at the distance 2r

$$U = \frac{6e^2(Z^+)(Z^-)}{kr} + \frac{12e^2(Z^+)^2}{k\sqrt{2}r} + \frac{8e^2(Z^+)(Z^-)}{k\sqrt{3}r} + \frac{6e^2(Z^+)^2}{k2r} + \ldots$$

$$U_{NaCl} = \frac{-ke^2|z|^2}{r} - \frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{2}} + \frac{24}{\sqrt{5}} \ldots$$

The sum is called the Madelung's constant, and it is characteristic and it is characteristic of the geometrical of the go arrangement and independent of the ions of their charges.

If we made (N ion pairs) of the compound MX, then NE would be the energy of the process.

$$M^+_{(g)} + X^-_{(g)} = MX_{(s)}$$

Thus NE is the electrostatic potential energy per mole for a hard-sphere ionic with NaCl structure.

We know that real atoms are not rigid spheres, and their equilibrium separation in are ionic must therefore be a consequence of some short-range repulsive force due to overlapping of their electron clouds which comes into play as they approach. Born proposed the simple assumption that the repulsive force between two ions could be represented by the expression B'/r^n in which B' and n are constant characteristic of their of the ion pair concerned.

The repulsive energy of a particular ion in a crystal:

$$E_{rep} = B/ r^n$$

where B is related to B' by the crystal geometry. The total electrostatic energy of the crystal, that is, the inherent negative lattice energy, U, is then given by:

$$U = N (Z^+)(Z^-)e^2A/r + B/r^n$$

A is the Madelung constant.

There is a relation between B and n which may be determined if we recognize that in the equilibrium state of the crystal($r = r_o$) the energy is a minimum as a function of r. Thus:

$$\frac{dU}{dr} = O = -\frac{A(Z^+)(Z^-)Ne^2}{r_0^2} \cdot \frac{-nB}{r_0^{n+1}}$$

which yields: $B = \frac{A(Z^+)(Z^-)e^2}{n} \cdot \frac{r_0^{n-1}}{1}$

and: $U = N (Z^+) (Z^-) A\frac{e^2}{r_0} (1\text{-}1/n)$

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To the lattice energy there are many contributions indicated in the Table 1

Table 1. Components of Lattice energy

Energy	LiF	NaCl	CsI
Coulomb	-12.4	-8.92	-6.4
Repulsion	+1.9	+1.03	+0.63
Van der Waals	-0.17	-0.13	-0.48
Zero point	+0.17	+0.08	

The calculation of lattice energy of ionic compounds is very important since, in general, there are no direct way to measure them experimentally although they can be obtained from certain experimental data using the Born- Haber cycle.

The Born -Haber cycle

The heats of formation of various ionic compounds show tremendous variations. In general, we know that many factors contribute to the over-all heat of formation namely, the ionization potentials, electronic affinity, heats of vaporization and dissociation of the elements, and the lattice energy of the compound .The Born-Haber cycle is a thermodynamic cycle which shows the interrelation of these quantities and enables us to see how variations in heats of formation can be attributed to the variations in these individual quantities.

In order to construct the Born-haber cycle we consider the following thermo chemical equations, using NaCl as an example:

$$Na_{(s)} = Na_{(g)} + \Delta H_{subl}(Na)$$

$$Na_{(g)} = Na^{+}_{(g)} + e^{-} + I_{Na}$$

$$1/2\ Cl_{2\,(g)} = Cl_{(g)} + 1/2\ \Delta H_{diss}(Cl_2)$$

$$Cl_{(g)} - e^{-} = Cl^{-}_{(g)} - A_{Cl}$$

$$Na^{+}_{(g)} + Cl^{-}_{(g)} = NaCl_{(s)} - U$$

$$Na_{(s)} + 1/2\ Cl_{2(g)} = NaCl_{(s)} \quad \Delta Hf \quad (NaCl)$$

Normally, ΔH_f, ΔH_{subl}, I and ΔH_{diss} are known. Direct measurement of electron affinities is usually rather difficult, and only for the halogens have really accurate values been obtained. Thus, the cycle is more commonly used for determine electron affinities. For example, the electron affinity of oxygen is a very important quantity which cannot be measured directly, if no other reason than that it is highly negative, namely -7.3 eV. This value has been obtained by applying the Born-Haber cycle to various ionic oxides.

Ionic Radii

It is already apparent from the nature of the wave functions for atoms and ions that they have no definite size. The only way we can assign a radius to an atom or ion is to measure in one way or another how two atoms or ions can approach one another under the influence of forces of the magnitude encountered in chemical processes. For the ions in a crystal we can do this by considering the distance between the centers of two adjacent ions to be the sum of their ionic radii. From X-ray measurements of the ionic distances in a large number of ionic radii can be completed.

One simple method for estimating the radius is based on the proposal that for a pair of isoelectronic ions, say Na^+ and F^- ,the radii will be inversely proportional to the effective nuclear charge to which the outer electrons are subject. According to the Slater's procedure, one obtains for the shielding of outer (2s, 2p) electron in the neon configuration the value 4.15. For Na^+ (Z=11) and

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$Z^* = 11 - 4.15 = 6.85$ which F^- (Z=9) and $Z^* = 9\text{-}4015 = 4.85$. Thus, the ratio of the radii $r\ F^-/r\ Na^+ = 4.85/6.85 = 0.71$.

If now the sum of these radii is taken as the Na-F distance in NaF (2.31A°), the individual radii must be $r\ F^- = 1.35A°$; $r\ Na^+ = 0.96A°$

Some Important Types of Ionic Lattices

A great ionic compounds of the type M^+X^- occur with one of three structures; the sodium chloride (see the FigureIV.1),the cesium chloride (figure 3) or zinc ZnS (Figure 3) structure.

In an ionic lattice each ion is surrounded by a certain number of ions of the opposite sign; this number is called the coordination number of the ion. In three structures mentioned the cations have the coordination numbers 6, 8 and 4, respectively.

The factors which contribute to the energy are the force between oppositely charged ions, which will increase with increasing coordination number, and the forces of repulsion, which will increase very rapidly if the ions of the same charge are squeezed together.

THEORETICAL TREATMENT OF THE COVALENT BOND

1. Valence Bond (Heitler-London Theory)

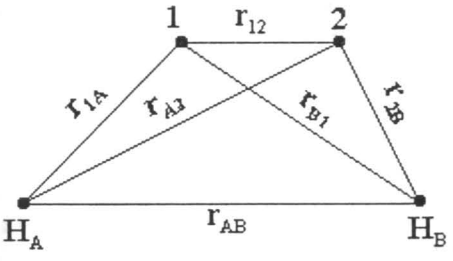
A hydrogen molecule H_2 is described by a wave function $\psi = \psi_A \cdot \psi_B$ when two hydrogen atoms are brought togeter without exchanging electrons (structure I), there is a weak attraction at large distances that becomes a strong repulsion at short distances. (The hydrogen nuclei are represented as H_A and H_B and the electrons as $\cdot$ 1 and $\cdot$ 2). Since a short distances the alternative structure, in which the electrons exchange positions (structure II) is just as likely, the potential energy curve (lower solid curve) corresponds to the normal H-H distance by the exchange between two equivalent structures, as in resonance stabilization.

$$I \quad H_A^{\cdot 12 \cdot} \quad H_B \qquad\qquad II \quad H_A^{\cdot 21 \cdot} \quad H_B$$

The wave functions for the individual structures can be written.

$$\Psi_I = \Psi_A(1)\,\Psi_B(2)$$
$$\Psi_{II} = \Psi_A(2)\,\Psi_B(1)$$

These functions must satisfy the Schrödinger equation $H\psi = E\psi$ where H isn't a simple number but a symbol which represents a sum of energies in the H_2 molecule.



$$H = \sum K.E. + \sum P.E. + \sum E.R. + EN.R.$$

$$K.E.(1) = -\frac{h^2}{2m}\left(\frac{d^2}{\partial x_1^2} + \frac{d^2}{\partial y_1^2} + \frac{d^2}{\partial z_1^2}\right)$$

$$P.E.(1) = \sum_x \frac{Z_x \cdot e}{r_{1,X}}$$

Z_X = nuclear charge of the X - atom

$r_{1,X}$ = the distance between the e_1 electron and the X nucleus.

$$E.R.(1,2) = \frac{e^2}{r_{1,2}^2} \qquad N.R.(AB) = \frac{Z_A \cdot Z_B}{r_{AB}}$$

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$$H = KE(1) + KE(2) + PE(1A) + PE(1B) + PE(2B) + PE(2A) + ER(12) + NR(AB)$$

$$H = 2H_0 + H_1$$

The wave function, which corresponds to this system, is obtained by L.C.A.O. method as a linear combination:

$$\psi_+ = c_1 \psi_I + c_2 \psi_{II}$$

$$\Psi_+ = c_1 \Psi_A(1)\, \Psi_B(2) + c_2 \Psi_A(2)\, \Psi_B(1)$$

and

$$\Psi_- = c_1 \Psi_A(1)\, \Psi_B(2) - c_2 \Psi_A(2) \Psi_B(1)$$

$$H_1 \Psi = E_1 \Psi$$

$$H_1 \Psi_+ = E_1 \Psi_+$$

$$\iint \Psi_+ H_1 \Psi_+ dv_1 dv_2 = E_I \iint \Psi_+ \Psi_+ dv_1 dv_2$$

$$\iint \left[c_1 \Psi_A(1)\, \Psi_B(2) + c_2 \Psi_A(2) \Psi_B(1)\right] H_1 \left[c_1 \Psi_A(1) \Psi_B(2) + c_2 \Psi_A(2) \Psi_B(1)\right] dv_1 dv_2 =$$

$$= c_1 \Psi_A(1) \Psi_B(2) H_1 c_1 \Psi_A(1) \Psi_B(2) dv_1 dv_2 + c_1 \Psi_A(1) \Psi_B(2) H_1 c_2 \Psi_A(2) \Psi_B(1) dv_1 dv_2 +$$

$$+ c_2 \Psi_A(2) \Psi_B(1) H_1 c_1 \Psi_A(1) \Psi_B(2) dv_1 dv_2 + c_2 \Psi_A(2) \Psi_B(1) H_1 c_2 \Psi_A(2) \Psi_B(1) dv_1 dv_2$$

$c_1 = c_2 = c$ because $H_A = H_B$ in the hydrogen molecule where K corresponds to the electrostatic energy and J corresponds to the exchange energy.

$$K = \iint \Psi_A(1)\, \Psi_B(2)\, H_1\, \Psi_A(1)\, \Psi_B(2) = \iint \Psi_A\, \Psi_B(1)\, H_1\, \Psi_A(2)\, \Psi_B(1)$$

$$J = \iint \Psi_A(1) \Psi_B(2) H_1 \Psi_A(2) \Psi_B(1) = \iint \Psi_A(2) \Psi_B(1) H_1 \Psi_A(1) \Psi_B(2)$$

Thus $\iint \Psi_I\, H_1 \Psi_1 dv_1 dv_2 = c^2(2K + 2J)$

$$E_I = \frac{c^2(2K + 2J)}{\iint \Psi_+ \Psi_+ dv_1 dv_2}$$

$$\iint \Psi_I\, \Psi_I\, dv_1 dv_2 = \iint \left[c_1 \Psi_A(1)\, \Psi_B(2) + c_2 \Psi_A(2) \Psi_B(1)\right]^2 \cdot dv_1 dv_2 =$$

$$= c_1^2 \iint \Psi_A^2(1) \Psi_B^2(2) dv_1 dv_2 + 2c_1 c_2 \iint \Psi_A(1)\, \Psi_B(2) \cdot \Psi_A(2)\, \Psi_B(1) dv_1 dv_2 +$$

$$+ c_2^2 \iint \Psi_A^2(2)\, \Psi_B^2(2) dv_1 dv_2 = c^2(2 + 2S)$$

because $\iint \Psi_A^2(1)\, \Psi_B^2(2)\, dv_1 dv_2 = \iint \Psi_A^2(2)\, \Psi_B^2(1)\, dv_1 dv_2 = 1$

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$\Psi_A(1), \Psi_B(2), \Psi_A(2), \Psi_B(1)$ are ortogonal function

$\iint \Psi_A(1)\,\Psi_B(2)\cdot\Psi_A(2)\cdot\Psi_B(1)\,dv_1 dv_2 = S^2$ named the superposition integral.

$$E^+ = \frac{(2K+2J)c^2}{\left(2+2S^2\right)c^2} = \frac{2K+2J}{\left(2+2S^2\right)} = \frac{K+J}{1+S^2}$$

The c_1c_2 coefficients can be determined from the maximum probability $\int \Psi_+^2 dv = 1$.

$$c_1^2\int \Psi_A^2(1)\Psi_B^2(2)\,dv_1 + c_1^2\int \Psi_A^2(2)\Psi_B^2(1)\,dv_1 + 2c_1^2\int \Psi_A(1)\,\Psi_B(2)\,dv_1\cdot\int \Psi_A(2)\,\Psi_B(1)\,dv_1 = 1$$

$$2c_1^2 + 2c_1^2\cdot S^2 = 1$$

$$2c_1^2\left(1+S^2\right) = 1$$

$$c_1^2 = \frac{1}{2\left(1+S^2\right)}$$

$c_1 = \dfrac{1}{\sqrt{2\left(1+S^2\right)}}$ and $c_2 = \dfrac{1}{\sqrt{2\left(1+S^2\right)}}$. The c_1, c_2 are mixing coefficients.

Similarly can be calculated the equation for $E_{II} = \dfrac{K-J}{1-S^2}$ corresponds to Ψ_{II}.

The total energy: $E_{tot} = 2E_0 + E_1^{\pm} = 2E_0 + \dfrac{K \pm J}{1 \pm S^2}$.

When two hydrogen atoms are brought together without exchanging electrons (structure I $H_A^{\cdot 12\cdot} H_B$ there is a weak attraction at large distances that becomes a strong repulsion at short distances (dashed curve Figure 21). Since at a short distances the alternative structure, in which the electrons exchange positions (structure II $H_A^{2\cdot\ \ 1\cdot} H_B$), is just as likely, the potential energy curve (lower solid curve) corresponds to the normal H-H distance by the exchange between two equivalent structures (I and II) as in resonance stabilization.

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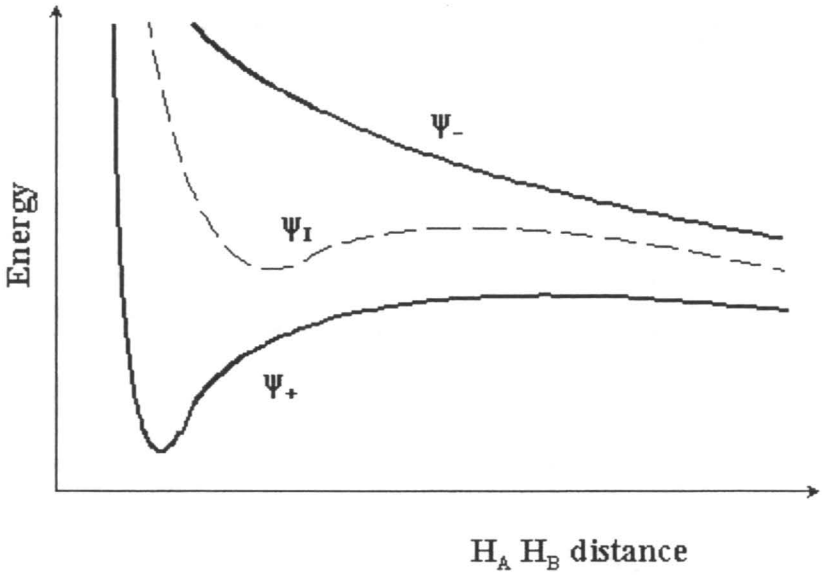

Figure 21 Potential - energy curves

The minimum in the potential energy indicates that the ψ_+ wave function leades to a stable molecule. The wave function $\Psi_- = c_1 \Psi_I - c_2 \Psi_{II}$ represents the situation in which no attraction is observed at any distance, because the two electrons have parallel spins (see the upper solid curve in Figure 21). Electrons must have oposed spins for favorable interaction. Pauling has shown that the results may be improved by a consideration of ionic structures for the hydrogen molecule. This results in the addition of two more terms to the wave equation.

Ionic structures	New terms to be added
III $H_A^{(+)}:H_B^{(-)}$	to the equation of ψ_+ named ψ_{ionic}
IV $H_A^{(-)}:H_B^{(+)}$	$\Psi_{ion} = c_3\Psi_B(1)\,\Psi_B(2) + c_4\Psi_A(1)\Psi_A(2)$

The hydrogen molecule can be characterized by a total wave function:

$$\Psi_{tot} = \left(1 - 2\lambda + 2\lambda^2\right)^{-1/2}\left[(1-\lambda)\Psi_+ + \lambda\Psi_{ion}\right]$$

In this equation ψ_+ corresponds to ψ covalent.

The Heitler-London treatment can be extended to other molecules with the covalent bond resulting from the interaction of electrons with opposed spins on two atoms. The valence electrons of a combining atom must be unpaired. If they are not unpaired in the ground state of the atom, vacant orbitals of low energy must be available to accommodate in separate orbitals the previously spin-paired electrons.

For second-period elements the atomic orbitals must be of the same major quantum number, n, because the orbitals must not differ greatly in energy. An atom can then from a covalent bond for each of its stable valence orbitals. Thus nitrogen with the outer configuration $2s^2 2p_x^1 2p_y^1 2p_z^1$ can from three bonds, as in NF_3, but cannot from NF_5, because the second shell can accommodate only light electrons.

Phosphorus with the configuration $3s^2 3p_x^1 3p_y^1 3p_z^1$ can from PF_3; and by promoting one 3s electron to a vacant 3d orbital to give the configuration $3s^1 3p_x^1 3p_y^1 3p_z^1 3d^1$, it can from five bonds in PF_5.

The Heitler-London treatment features the formation of a chemical bond as the result of the pairing of two electrons, one form each bonded atom. The electron density of the shared pair is a maximum between the two bonded atoms. The Heitler-London treatment does not consider the formation of odd-electron molecules H_2^+, where no pairing occurs, and it doesn't include the

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formation of the coordinate covalent bond where one of the bonded atoms furnishes both of the electron pairs.

2. Valence Bond (Pauling-Slater) Theory Overlap of Atomic Orbitals

The main consideration is that stable compounds result from the tendency to fill all stable orbitals with electron pairs, shared or unshared.

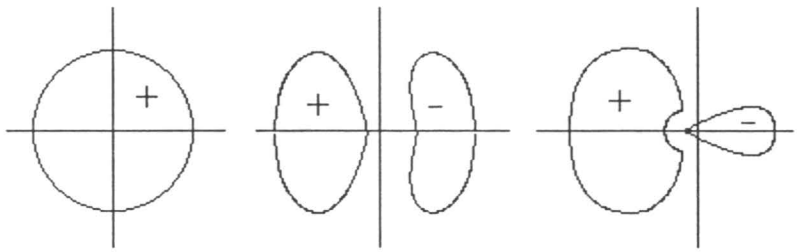
A covalent bond may be described as resulting from the overlap of orbitals on two atoms so that the two orbitals can be occupied by an electron pair. In HF the spherically symmetrical s orbital of H overlaps with the singly occupied 2p orbital of F.

The shape of a molecule is determined primarily by the directional characteristics of the orbital involved. But there are many molecules (e.g. H_2O, NH_3), which do not obey the bond angle of the involved orbitals. For example the H_2O molecule results from the overlap of the two singly occupied p orbitals of oxygen with the s orbital of each of two hydrogen atoms, to from an angular molecule (see Figure 22a). The p orbitals are mutually perpendicular, but the bond angle in water is 104.45^0. Repulsion between the hydrogen atoms only, doesn't accounts for the fact that the angle is greater than 90^0. The ammonia molecule is pyramidal with a bond angle of 107.3^0, while the three p orbitals of the nitrogen atom are mutually perpendicular. In the methane CH_4 molecule the outer configuration of the carbon atom must be $2s^1 2p_x^1 2p_y^1 2p_z^1$ and no $2s^2 2p_x^1 2p_y^1$. These characteristic aspects of the molecules can be explained by means of the by hybridization theory (Pauling-Slater).

Hybridization

The process of combining atomic orbitals to give mixed orbitals is known as hybridization. In the second period there are four kind of combining **s** an **p** orbitals.

(i) The combination of the **s** and three **p** orbitals gives tetrahedral hybrid $\mathbf{sp^3}$ orbitals. The **p** lobe with the same sign of the ψ function as that of the **s** orbital is enlarged, and the one of opposite sign is diminished. The enlarged lobe of the resulting orbital can give more favorable overlap with the orbital of another atom and thus from a stronger bond than can either the **p** or **s** orbitals alone. The orbital represented is one of the four equivalent $\mathbf{sp^3}$ orbitals.



s **p** **sp³**

(ii) There are three equivalent $\mathbf{sp^2}$ hybrid orbitals and

(iii) two equivalent **sp** orbitals.

The shapes of the major lobes $\mathbf{sp^3}$, $\mathbf{sp^2}$, **sp** hybrid orbitals differ very little, mainly in the relative sizes of the minor and major lobe. The minor lobe is largest for $\mathbf{sp^3}$ and smallest for **sp**, so the greatest fraction of electron density would be in the bonding lobe for the **sp** hybrid orbital. Overlap integrals increase in the order $\mathbf{sp^3} < \mathbf{sp^2} < \mathbf{sp}$, indicating the greatest overlap for **sp** bonds.

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The increasing C-H bond energies in the series CH_4,C_2H_4, C_2H_2 support increasing bond strengths with increasing s character for sp^2 hybrid - that is, greatest for **sp**.

Pauling used the extension of the orbitals, rather than the overlap integrals, to arrive at a different order of relative bond strengths: 1.93 for **sp**, 1.99 for sp^2, 2.00 for sp^3, compared with 1.00 for pure **s**. The overlap integrals provide better estimates of bond strengths.

Figure 23 displays some of the important hybrids - including cases involving **d** orbital participation - along with the corresponding geometrical configurations.

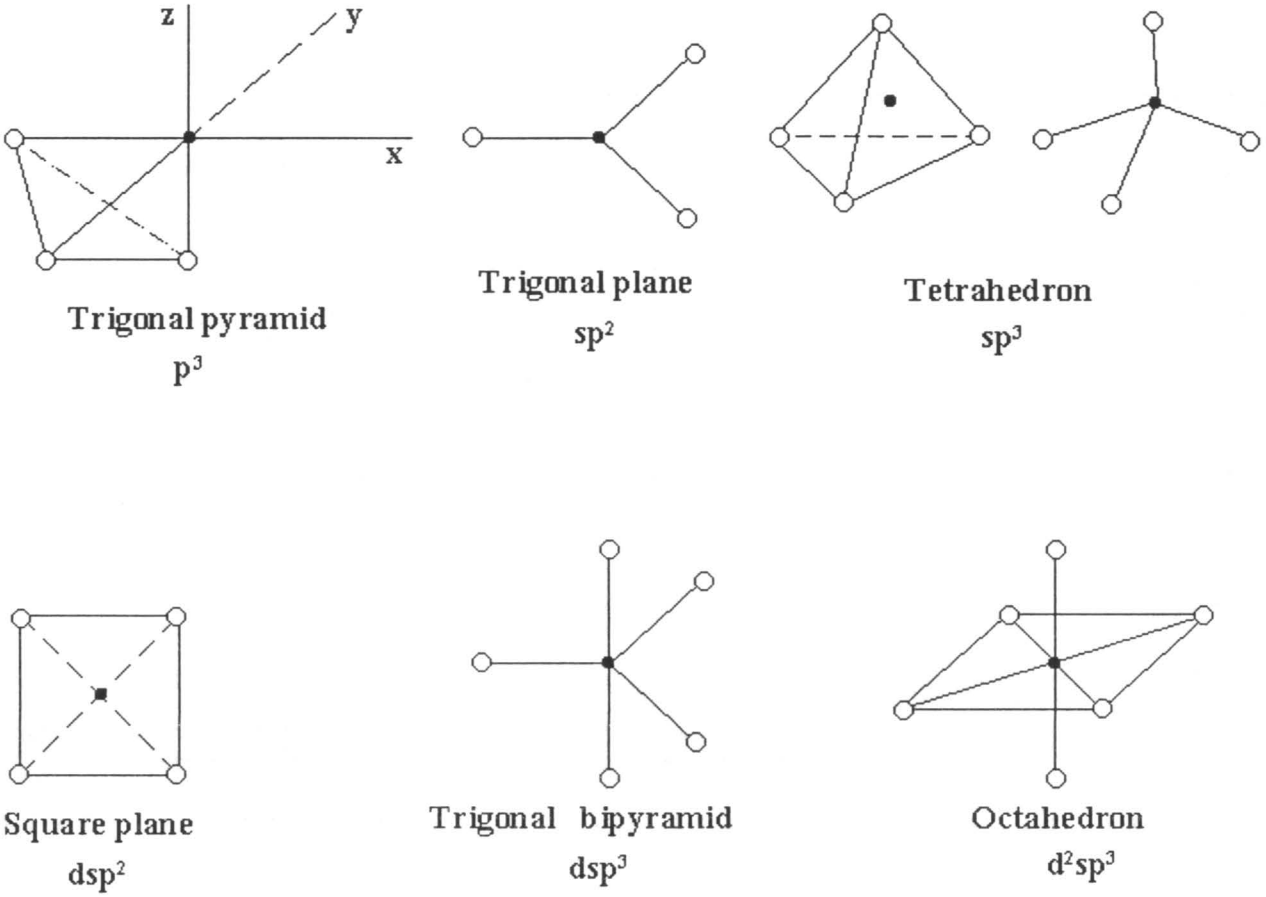

Figure 23 Some bonding configuration

3 Shapes of Molecules. Molecular Geometry and Hybridization

The shape of a molecule, to a first approximation, is determined by its σ bond structure. Since they often occupy hybridized orbitals, unshared electron pairs, can be treated as bouded groups in determining the hybridization: accordingly, the hybridization in NH_3 and H_2O can be considered to be sp^3. The importance of unshared electron pairs in determining molecular shapes is illustrated in Table 5.

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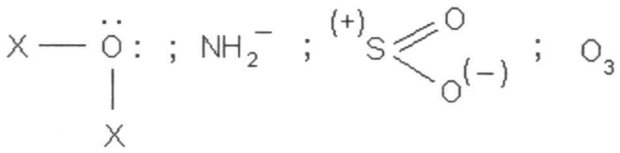
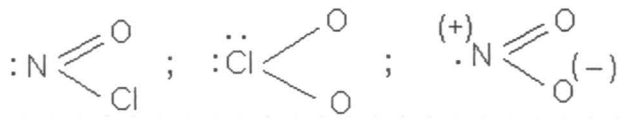
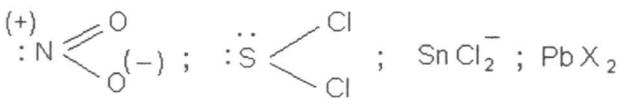
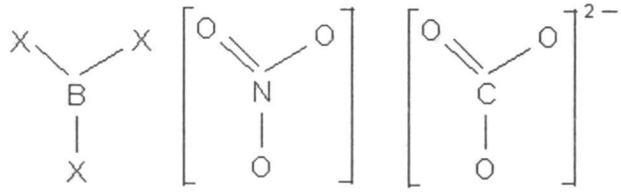
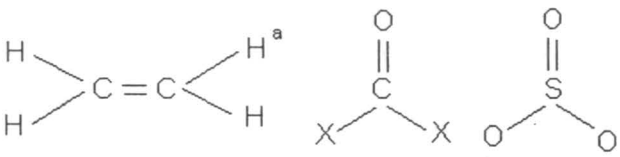
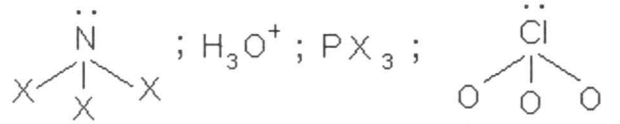
Table 5 Shapes of some simple molecules

General Formula	Number of Unshared Electrons on A	τ Bonding Orbital Hybridization	Shape	Examples
AX_2	none	sp	Liniar	O=C=O; S=C=S; $O=N^+=O$; H-C≡N; CH≡CH; ZnX_2; CdX_2; $AgCl_2^-$; HgX_2
	one or more	sp^2 or sp^3	Angular	 ; NH_2^- ; ; O_3
				
				
AX_3	none	sp^2	Planar	
				
	one or two	sp^3	Pyramidal	 ; H_3O^+ ; PX_3 ;
AH_4	none	sp^3	Tetra-hedral	CX_4; NH_4^+; BX_4^- ; SiX_4; TiX_4; ZnX_4^{2-}; SO_4^{2-}; SO_2Cl_2; POX_3; PO_4^{3-} ; ClO_4^-

In many molecules it is difficult to assess a priori the relative importance of various contributing structures or the contribution of a particular type of hybridization. Atoms with more low-lying orbitals than valence electrons will have reasonably unambigous σ bond configurations and hence predictable structures. Atoms with more valence electrons than low-lting orbitals may contribute these electrons in varying degrees in diverse situation, and accordingly, may have several distinct and not easily available σ bond structures. For example in trimethoxoboron, $B(OCH_3)_3$, molecule the boron hybridization must be **sp^2** with bond angles 120^0, but the orbital hybridization of the oxygen must be intermediate between **sp^3**and **sp^2** (Figure 24). Hence double bonding would favor **sp^2** hybridization here. Similarly the P-N bond in H_2N-PH_2 might be **sp^2**, **sp^3** or some

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intermediate combination of N orbitals. The hybridization of the σ bonding orbitals of each nitrogen in N_2O_5 must be **sp^2**, but the bridging oxygen might be **sp^3**, **sp^2**, or even **sp**.

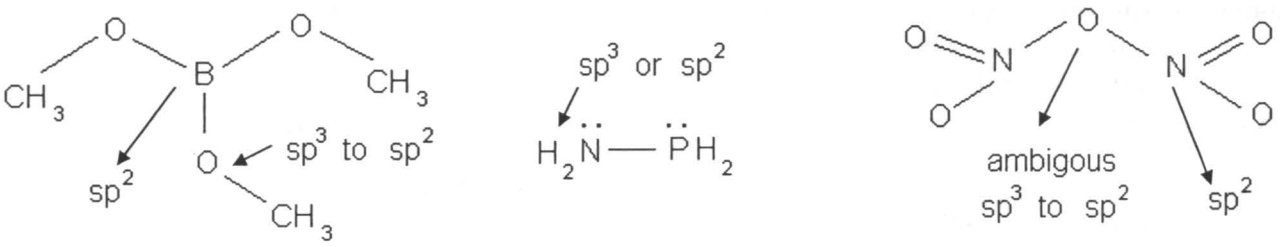

Figure 24 Possible assignments of hybridization

The geometry of a molecule in an excited electronic state likely will differ drastically from that of the ground state, as the promotion of an electron can charge the hybridization of the orbitals.

4. The Pauli Exclusion Principle and the Prediction of the Shapes of Molecules(Valence Shell Electron-Pair Repulsion Theory)

You can predict the approximate shapes of simple molecules by considering unshared electron pairs (lone pairs) to be equivalent to bonded groups. To obtain more exact descriptions of the molecular shapes and variations of bond angles, you must take into account repulsion among electron pairs in the valence shell of the central atom. Repulsion between bonding pairs is not as great as repulsion between lone pairs. This approach was introduced by Gillespie and Nyholm and developed extensively by Gillespie as the valence shell electron pair repulsion (VSEPR) theory.

If one of the electron pairs is used for bonding, as in HF, the four pairs are no longer equivalent. The bonding pair now becomes more localized, since its electrons are restricted in their motion by two positive nuclei. If two electron pairs are used for bonding, as in H_2O, the bond angle will be determined by the repulsions among the four electron pairs. Instead of the normal tetrahedral angle (109.47^0) for four equivalent pairs, as found in CH_4 and as expected for O^{2-}, the bond angle in H_2O is 104.45^0.

The repulsion between electron pairs decreases in the order

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

In NH_3 the HNH bond angles are 107.3^0 - an angle greater than that in H_2O because there are no lone pair-lone pair repulsions.

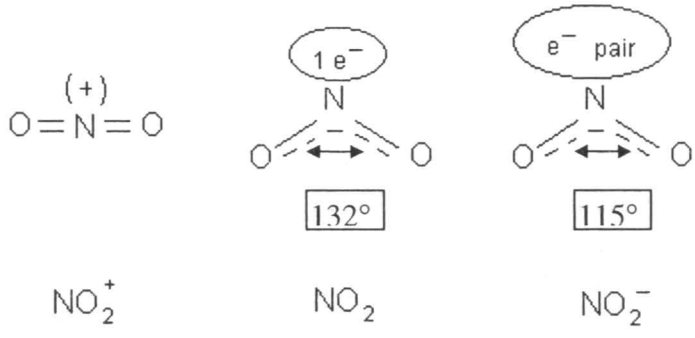

Figure 25 Bond angles in NO_2^+, NO_2, NO_2^-

Comparing the bond angles in NO_2 (132^0) and in NO_2^- (115^0) demonstrates that a single unshared electron causes less repulsion than an unshared electron pair. The nirtyl ion, NO_2^+, with no unshared electron on nitrogen, is linear (see Figure 25).

The non angles decrease in the series NH_3, PH_3, AsH_3, SbH_3 and in the series H_2O, H_2S, H_2Se, H_2Te (see Table), presumably because the increasing size and lower electro-negativity of the central atom permit the bonding electrons to be drawn out further, thus decreasing the repulsion between bonding pairs. The variation in bond angles is in the direction expected for are increase in the bonds' **p** character: that is, the bond angles approach the values expected for **p^3** bonds, rather than

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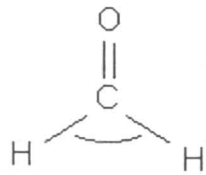
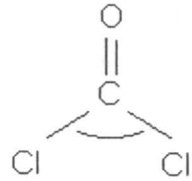
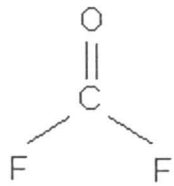
those for sp^3 hybrid bonds. This is just the opposite of what might be expected, since the energy difference between the **s** and **p** orbitals is greatest for nitrogen.

The bond angles decrease by large amounts from NH_3 to PH_3 or from H_2O to H_2S, then by very small amounts for the following members of each series.

Gillespie suggests that the difference arises because N and O are members of the second period, for which the octet represents a closed shell. Strong repulsions between the electron pairs result from the fact that the space around the central atom is filled completely. For compounds of elements of the second period, the bond angles really fall below the tetrahedral angle by more than a few degrees. Members of the later periods can accommodate more than four electron pairs in the valence shell; the maximum usually is six pairs. Six electron pairs in the valence shell of an atom should produce an octahedral arrangement with angles of 90^0 between electron pairs, and the bond angles of the hydrides of the heavier group V and VI elements do seem to approach 90^0 (see Table 6).

The decrease in the bond angles for NF_3 and F_2O as compared with NH_3 and H_2O may be explained in terms of the decrease in repulsion between bonding pairs resulting from the electrons being drawn out further by the fluorine. The FCF bond angles in the C-F compounds shown in the Table 6 are also smaller than HCH bond angles in the corresponding C-H compounds. The bond angles of the fluorine compounds are smaller than those of the corresponding hydrogen compounds only for second-period elements.

Table 6 Comparison of bond angles

CH_4		109.47^0			
CH_3F	HCH	110^0			115.8^0
CH_3Cl	HCH	110.3^0			
CHF_3	FCF	108.8^0			111.3^0
$CHCl_3$	ClCCl	110.4^0			108.0^0

NH_3	107.3^0	NF_3	102.4^0	NCl_3	106.8^0	Pbr_3 101.0^0
PH_3	93.3^0	PF_3	97.8^0	PCl_3	100.1^0	PI_3 102^0
AsH_3	91.8^0	AsF_3	96.2^0	$AsCl_3$	98.5^0	
SbH_3	91.3^0	SbF_3	95.0^0	$SbCl_3$	97.2^0	

5. MOLECULAR ORBITAL THEORY OF COVALENT BONDING

In (V.B.T) electron pairs are localized between particular pairs of nuclei, and the wave function for these electrons is just the products of atomic wave functions.

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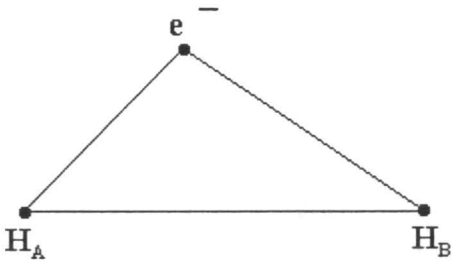
The M.O. theory in building up a multi-electron atom started with a nucleus and a set of one-center orbitals about that nucleus and fed the required number of electrons into these orbitals by solving exactly the problem with only one electron and then assumed that when many electrons are present the orbitals have the same form but that their relative energies are affected by the shielding of one electron by another. In other words, we treat each electron as if it moves in the effective field produced by the nucleus and all of the other electrons.

The LCAO method is a simple and qualitatively useful approximation. To develop this idea more concretely we shall use the hydrogen molecule ion H_2^+. This is a prototype for homonuclear diatomic molecules just as the hydrogen atom is for atoms in general.

If the electron belonged to either of hydrogen nuclei A or B alone, its behavior in the ground state would be described by ϕ_A or ϕ_B alone. When it is in some general position with reference to the nuclear framework it can be approximately described by a superposition of both, that is, by $\Phi_A \pm \Phi_B$. Such an algebraic sum of functions is called a linear combination. The two normalized LCAO wave functions written out fully are H_2^+.



$$\Psi_b = c_1 \Phi_A + c_2 \Phi_B$$

$$\Psi_a = c_1 \Phi_A - c_2 \Phi_B$$

$$H \Psi = E \Psi$$

$$\Psi H \Psi = E \Psi^2$$

$$\int \Psi H \Psi dv = E \int \Psi^2 dv$$

$$\int \Psi_b H \Psi_b dv = E \int \Psi_b^2 dv$$

$$E_b = \frac{\int \Psi_b H \Psi_b dv}{\int \Psi_b^2 dv} = \frac{\int (c_1 \Phi_A + c_2 \Phi_B) H (c_1 \Phi_A + c_2 \Phi_B) dv}{\int (c_1^2 \Phi_A^2 + 2c_1 c_2 \Phi_A \Phi_B + c_2^2 \Phi_B^2) dv} =$$

$$= \frac{c_1^2 \int \Phi_A H \Phi_A dv + c_1 c_2 \int \Phi_A H \Phi_B dv + c_2 c_1 \int \Phi_B H \Phi_A + c_2^2 \int \Phi_B H \Phi_B dv}{c_1^2 \int \Phi_A^2 dv + 2c_1 c_2 \int \Phi_A \Phi_B dv + c_2^2 \int \Phi_B^2 dv} =$$

$$\left.\begin{aligned} \int \Phi_A H \Phi_A dv &= H_A \\ \int \Phi_B H \Phi_B dv &= H_{BB} \end{aligned}\right\}$$ coulombien integrals

$$\left.\begin{aligned} \int \Phi_A H \Phi_B dv &= H_{AB} \\ \int \Phi_B H \Phi_A dv &= H_{BA} \end{aligned}\right\}$$ change integrals

$$\left.\begin{aligned} \int \Phi_A^2 dv &= S_{AA} \\ \int \Phi_A \Phi_B dv &= S_{AB} \\ \int \Phi_B^2 dv &= S_{BB} \end{aligned}\right\}$$ the overlap integrals

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$$E_b = \frac{c_1^2 H_{AA} + 2c_1c_2H_{AB} + c_2^2 H_{BB}}{c_1^2 S_{AA} + 2c_1c_2S_{AB} + c_2^2 S_{BB}}$$

In variational method $\frac{\partial E}{\partial c_1} = 0$ and $\frac{\partial E}{\partial c_2} = 0$

$$2c_1H_{AA} + 2c_2H_{AB} = E(2c_1S_{AA} + 2c_2S_{AB})$$
$$2c_2H_{BB} + 2c_1H_{AB} = E(2c_2S_{BB} + 2c_1S_{AB})$$

$$c_1(H_{AA} - ES_{AA}) + c_2(H_{AB} - ES_{AB}) = 0$$
$$c_1(H_{AB} - ES_{AB}) + c_2(H_{BB} - ES_{BB}) = 0$$

The solutions of the system are nonzero if

$$\begin{vmatrix} H_{AA} - ES_{AB} & H_{AB} - ES_{AB} \\ H_{AB} - ES_{AB} & H_{BB} - ES_{BB} \end{vmatrix} = 0$$

The solutions of the system are obtained after two successively approximations regard to

(i) $S_{AB} = 0$ and (ii) $S_{AB} \neq 0$

The overlap between a pair of atomic orbitals, S, is given by the equation $S = \int \Psi_A \Psi_B \, d\tau$ and S is called the overlap integral. This integral may have a value, which is positive, negative or exactly zero. When its value is positive, there is a built-up of electronic charge between the nuclei and bond can be formed. When the overlap integral is negative, there is a reduction in the electron density between the nuclei. This increases the repulsion between them and they tend to move aport. When the overlap is zero, there is no net interaction, attractive or repulsive.

Examples are presented in Figure 26. The overlaps shown in (a) -(d) are all positive, in (e) -(h) are negative while those in (i) - (l) are zero.

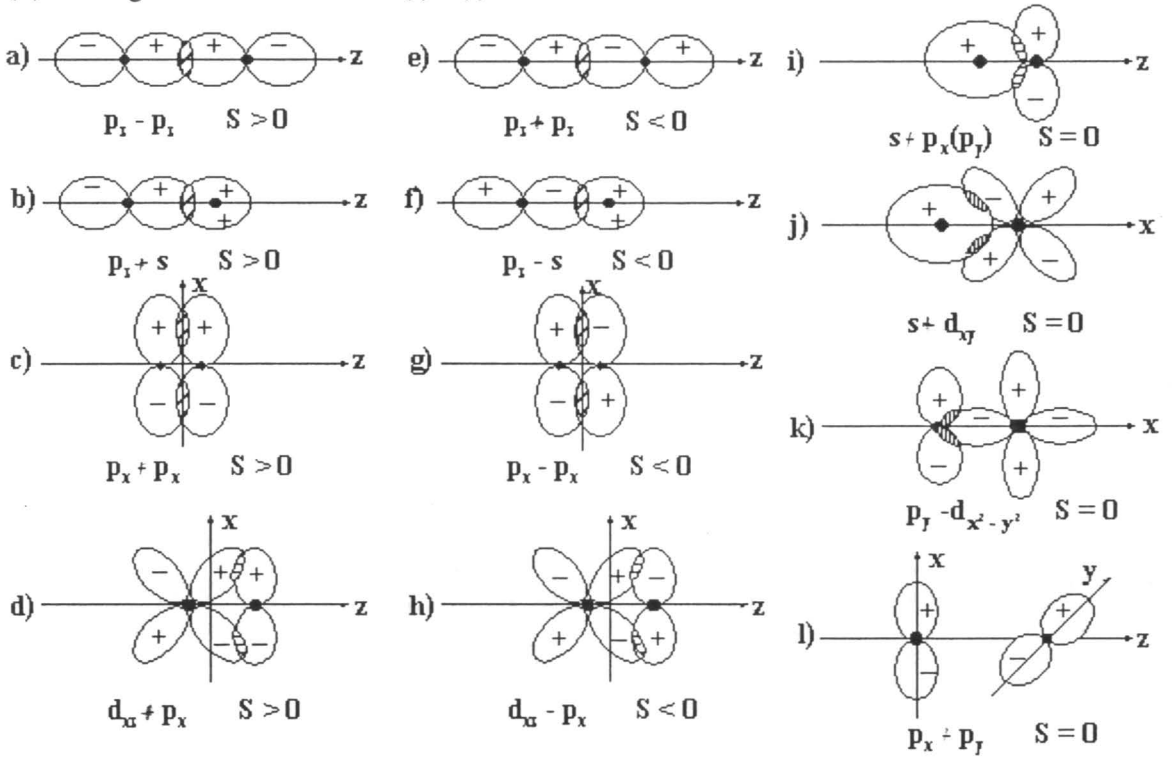

Figure 26 - Some reprezentative positive, negative and zero overlaps

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It is often desirable to estimate the magnitude of S. This can be done by expressing Ψ_A and Ψ_B in equation: $S = \int \Psi_A \Psi_B \, d\tau$ and carrying out the integration. Usually it is used the radial factor R(r) of the Ψ_A and Ψ_B, which were proposed many years ago by Slater.

$$R(r) = N r^{n-1} e^{\mu r/a_H}$$

where **N** is a normalizing factor, **n** is the principal quantum number, $\mathbf{a_H}$ is the Bohr radius and μ is a function of the effective nuclear charge for an electron in the orbital concerned.

Orbitals, which use the usual angular factors obtained by solving the wave equation for hydrogen together with these simple radial functions, are called Slater-Type Orbitals (STO's). The overlaps computed using single STO's are rough approximations by comparison with Hartree-Fock method.

However, it is possible to take linear combinations of a few STO's so as to approximate very closely the true shape of an orbital (Figure 27)

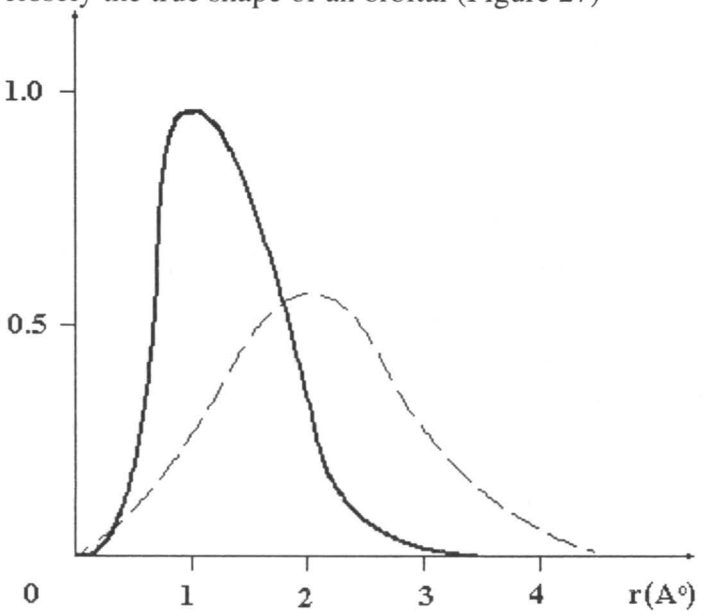

Figure 27 - A comparison of a Hartree-Fock 3d wave function for the Cr^{3+} ion (_____) with a Slater Type wave function (·····)

In H_2^+ molecule in the first approximation. (i) $S_{AB} = 0$; $H_{AA} = H_{BB} = \alpha$ (A and B are identically atom)

$S_{AA} = S_{BB} = 1$ (for ortogonale functions)

$H_{AB} = H_{BA} = \beta$

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

$\alpha^2 - 2E\alpha + E^2 - \beta^2 = 0$

$E^2 - 2\alpha E + \alpha^2 - \beta^2 = 0$

$(E - \alpha)^2 - \beta^2 = 0$

$(E - \alpha - \beta)(E - \alpha + \beta) = 0$

$E_b = \alpha + \beta$

$E_a = \alpha - \beta$

For $E_b = \alpha + \beta$

$c_1(\alpha - E_b) + c_2\beta = 0$

$c_1(\alpha - \alpha - \beta) + c_2\beta = 0$

$c_1(\alpha - \alpha - \beta) + c_2(\alpha - \alpha - \beta) = 0$

$\Rightarrow c_1 = c_2$

For $E_a = \alpha - \beta \Rightarrow c_1 = -c_2$

We know that Ψ_A and Ψ_B are orthonormale functions and

$$\int \psi_A \psi_B \, d\tau = 1 \qquad A = B$$

$$\int \psi_A^2 \, d\tau = 1$$

$$\psi_a = c_1\phi_A + c_2\phi_B$$

$$c_1^2 \int \phi_A^2 \, d\tau + 2c_1c_2 \int \phi_A\phi_B \, d\tau + c_2^2 \int \phi_B^2 \, d\tau = 1$$

$$S_{AA} = 1 \qquad S_{AB} = 0 \qquad S_{BB} = 1$$

$$c_1^2 + c_2^2 = 1 \quad \text{but} \quad c_1 = c_2 \quad \text{for} \quad E_b$$

$$2c_1^2 = 1 \qquad c_1 = c_2 = \frac{1}{\sqrt{2}}$$

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and $c_1 = - c_2$ for E_a

$$c_1 = \frac{1}{\sqrt{2}} \quad \text{and} \quad c_2 = - \frac{1}{\sqrt{2}}$$

$$\psi_b = \frac{1}{\sqrt{2}} (\phi_A + \phi_B)$$

$$\psi_a = \frac{1}{\sqrt{2}} (\Phi_A - \Phi_B)$$

In order to understand the physical meaning of the two LCAO- MO's let us first examine Figure 28. The solid lines show ψ_a^2 and ψ_b^2, the squares being used because we are at the moment chiefly interested in how the electron density is distributed along the internuclear line. The dotted lines show the electron density in the individual atomic orbitals, that is, they show Φ_a^2 and Φ_b^2. As a further indication of the significance of ψ_a^2 and ψ_b^2, they may also be compared with the dashed line, which is a plot of $\sqrt{1/2}\ \Phi_a^2 + \sqrt{1/2}\ \Phi_b^2$. This function gives the distribution of one electron spending its time equally in Φ_A and Φ_B, these remaining, however, as separate atomic orbitals. The factors of $\sqrt{1/2}$ normalize the total electron density in each Φ to 1/2. The subscript **b**, meaning bonding, and the subscript **a**, meaning anti-bonding.

Now the integral α is obviously just the energy of an electron in the orbital Φ_A or Φ_B , that is, it is equal to the ground state energy of the hydrogen atom. The integral β represents the energy of interaction between the orbitals Φ_A and Φ_B. It is called an exchange integral or resonance integral, and it can be shown that it is inherently negative. Thus an electron occupying the bonding MO, Ψ_b, is more stable and an electron in Ψ_a is less stable than one in a pure atomic orbital, Φ_A or Φ_B. The actual energies as stabilization and destabilization can be obtained in units of β by inserting the normalization coefficients.

If we make the approximation that overlap can be ignored, so that $c_1^2 = c_2^2 = 1/2$, we find that:

$$E_a = \alpha + \beta \quad \text{and} \quad E_b = \alpha - \beta$$

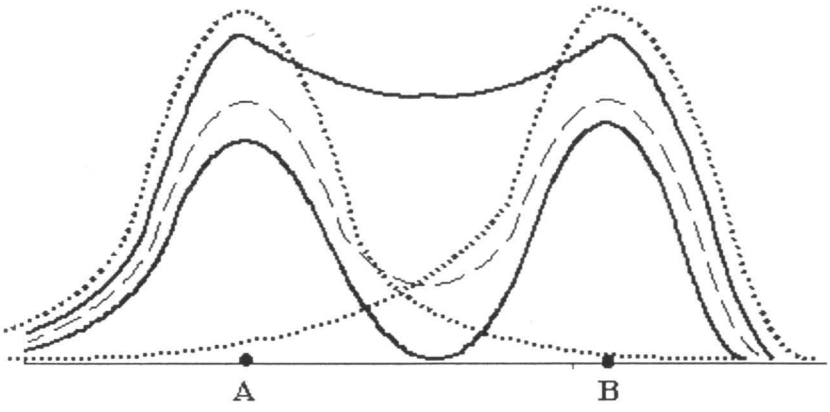

Figure 28
.....) ϕ_A^2, ϕ_B^2 The atomic orbital electron probabilities
—) ψ_a^2 and ψ_b^2 the molecular orbital electron probabilities
---) distribution of a single electron equally distributed over ϕ_A and ϕ_B along he intermolecular line for H_2^+. including overlap

These results are expressed in the energy level diagram, Figure 29. The atomic orbitals of the constituent atoms are placed on each side, and the resulting MO's are placed in the center. It is to be noted that when the overlap is included in the normalization coefficients, the problem becomes more complicated algebraically and the energy level diagram no longer possesses the simple, symmetrical form of Figure 29.

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In general, the larger the value of S for two orbitals Φ_A and Φ_B on two atoms, the stronger would be the bond which is formed using these orbitals.

Mulliken proposed that integrals β should be roughly proportional to the corresponding overlap integrals. It is also necessary to build into the relation expressing this proportionality a dependence on the overage value of the energies of the orbitals, which are forming the bond. Thus the following general equation is written:

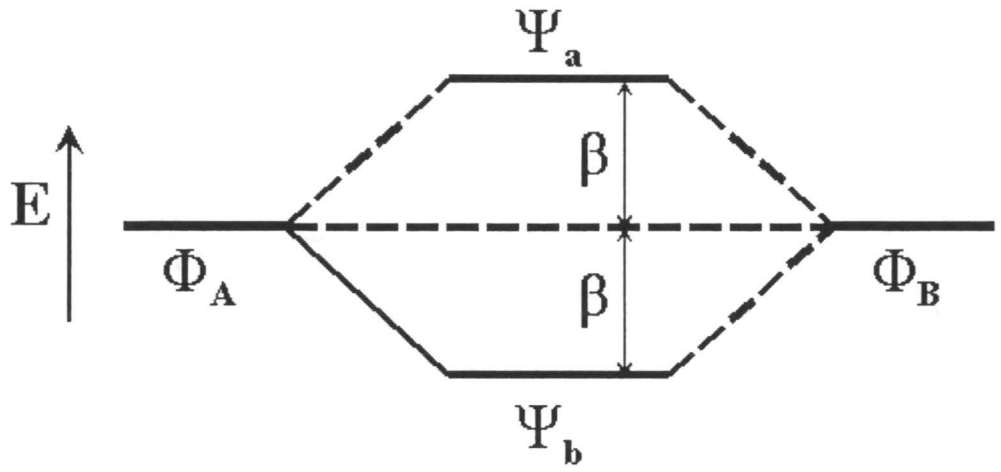

Figure 29 - Energy level diagram showing the formation of bonding and antibonding MO's from two equivalent atomic orbitals in a homonuclear diatomic molecule

$$\int \Phi_A H \Phi_B \, d\tau = \beta = C \beta_{av} S = C \beta_{av} \int \Phi_A \Phi_B \, d\tau$$

$$\beta_{av} = (\beta_A + \beta_B)/2$$

$$\text{or } \beta_{av} = (\beta_A \times \beta_B)^{1/2}$$

geometrical overage $C \cong 2.0$.

Bond Orders: The bond order is defined in MO theory as the number of electron pairs occupying bonding MO's minus the number of electron pairs occupying anti-bonding MO's.

Homonuclear Diatonic Molecules

These four orbitals can accommodate eight electrons, but, as in the case of helium, the molecule (Be_2) would be unstable. on the other hand, the Li_2 molecule, with the configuration $(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2$ should exit, and indeed lithium vapor although to a large extent monoatomic does contain a small fraction of diatomic lithium molecules.

When **p** orbitals are combined it is necessary to take into account their orientation with respect to each other. If the nuclei of the two atoms are assumed to lie on the *x* axis, then overlapping of the $\mathbf{2p_x}$ orbitals with each other produces σ molecular orbitals as shown in Figure 1.19. The bonding orbital, labeled **σ2p**, arises if the overlapping lobes are chosen to have same sign of Ψ, the anti-bonding orbital, labeled $\mathbf{\sigma^*2p}$, arises if the sign of Ψ in one lobe is positive and in the other, overlapped, lobe is negative, since this situation leads to a reduction in electron charge density in the region of space near to where Ψ passes through zero.

The sideways overlapping of the $\mathbf{2p_2}$ orbitals (or $\mathbf{2p_y}$ orbitals) results in molecular orbitals of a different kind (Figure 1.20). These are π (pi) molecular orbitals: $\pi_z\mathbf{2p}$ and $\pi^*_z\mathbf{2p}$ (or $\pi_y\mathbf{2p}$ and $^*_y\mathbf{2p}$). They are important in considerations of multiple bonding( ).

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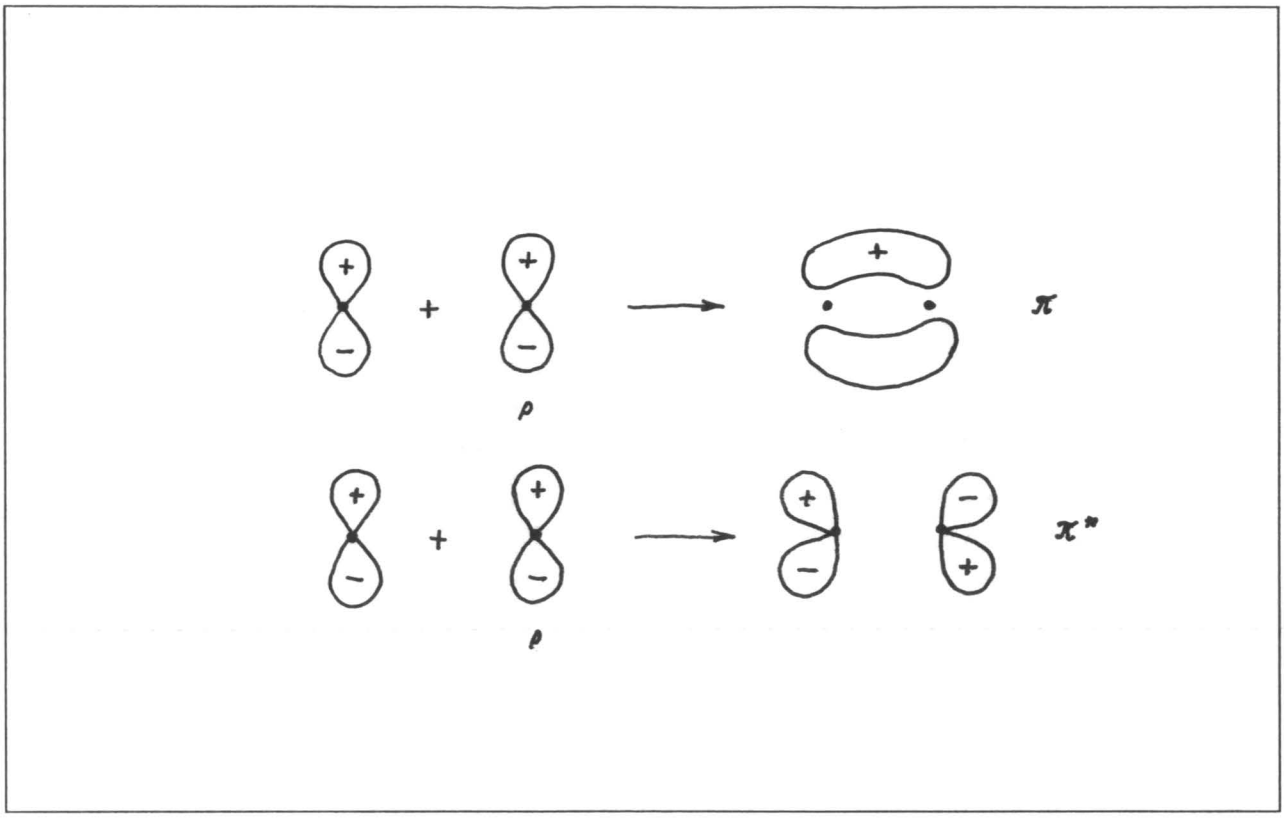

Figure - Sideways overlapping of **p** orbitals resulting in *(a)* π bonding orbital, and *(b)* π^* antibonding orbital

For simple diatomic molecules of the first ten elements, the energy sequence of molecular orbitals is (with one or two exceptions) as follows:

$$\sigma 1s,\ \sigma^* 1s,\ \sigma 2s,\ \sigma^* 2s,\ \sigma 2p,\ \pi_z 2p = \pi_z 2p,\ \pi^*_z 2p = \pi^*_z 2p,\ \sigma^* 2p$$

Each orbital will accommodate a pair of electrons. Complete filling of all ten orbitals would occur for the hypothetical Ne_2 Molecule, but no bonding would result because of complete cancellation between bonding and anti-bonding orbitals. In the case of the fluorine molecule (eighteen electrons), the bonding due to the **σ2p** orbital is not cancelled by the **σ^*2p** orbital because the latter orbital is empty. The fourteen electrons in the nitrogen molecule lead to the configuration

$$(\sigma 1s)^2\ (\sigma^* 1s)^2\ (\sigma 2s)^2\ (\sigma^* 2s)^2\ (\sigma 2p)^2\ (\pi_y 2p)^2\ (\pi_z 2p)^2$$

Bonding is due to three pair of electrons which constitute one σ bond and two π bonds. The multiple character of this bond, or the bond order, corresponds to a triple bond. The carbon monoxide molecule is isoelectronic with the nitrogen molecule and it possesses a similar configuration. The oxygen molecule contains two more electrons than the nitrogen molecule.

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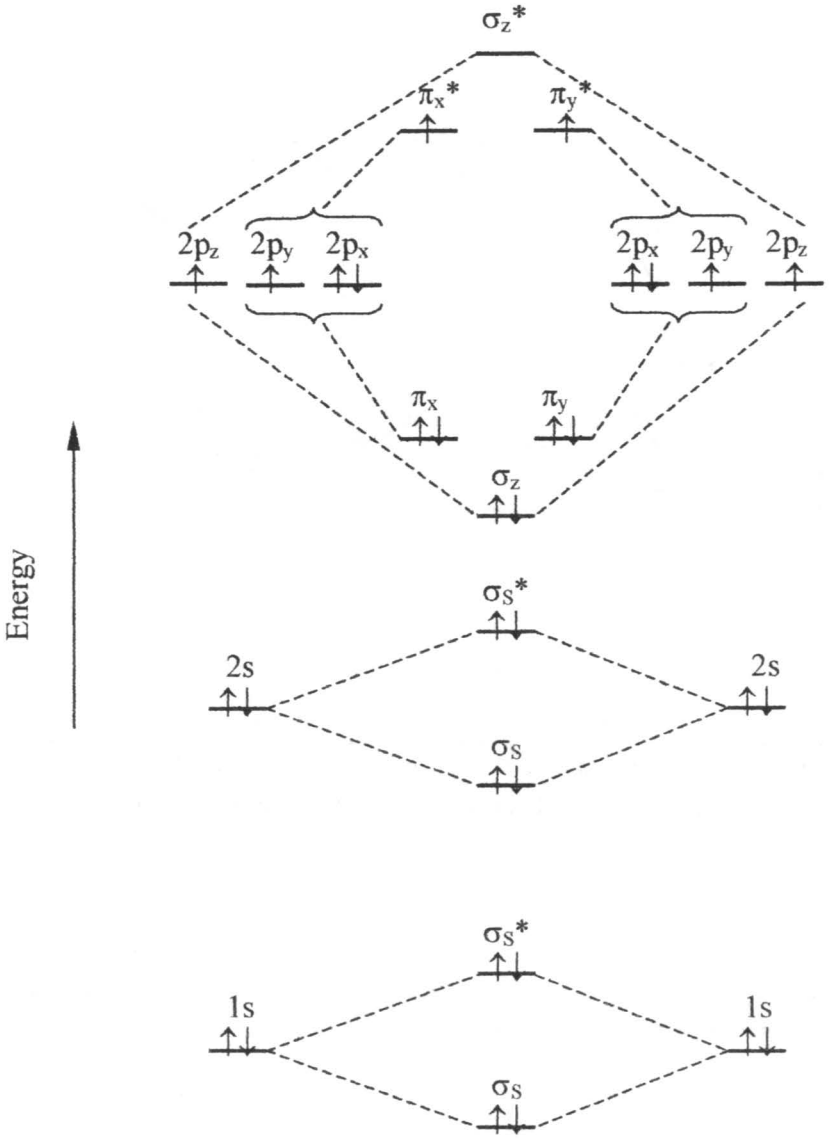

Figure – Electronic configuration of two separate oxygen atoms (left and right – hand columns) and of the oxygen molecule (center column).

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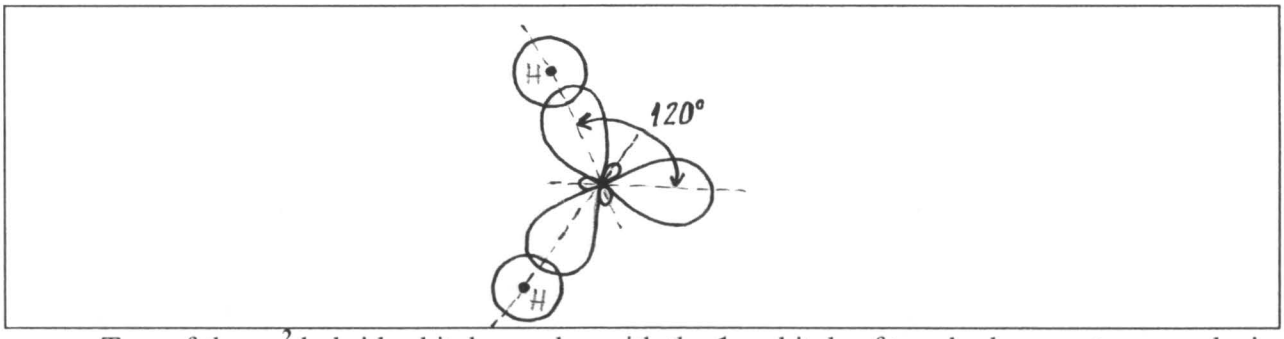
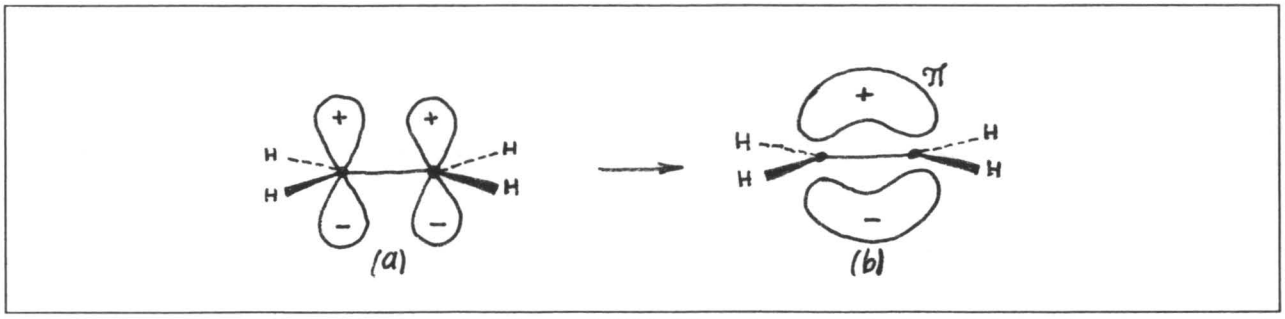
These are distributed in the π_y^***2p** and π_z^***2p** orbitals. Since these are anti-bonding orbitals, it follows that in the oxygen molecule the bond order is two. In accordance with Hund's rule of minimum pairing the two to electrons remain unpaired as indicated in Figure 1.21. Nitric oxide, with fifteen electrons (one less than O_2 but one greater than N_2) possesses one unpaired electron in the anti-bonding π level.

In accounting for simple σ bonding between atoms, both the molecular orbital theory and the valence bond theory make use of a pair of electrons; it is necessary that they are of opposite spin so as to comply with the Pauli exclusion principle. This applies not only to diatomic molecules but to poliatomic molecules generally. Multiple bonding arises when the σ bond is supplemented by other types of bonds such as π bonds. We have already seen in terms of the molecular orbital theory how, for diatomic molecules, the sideways overlapping of **p** orbitals gives to π bonding. When we consider multiple bonding in more complicated molecules it is often convenient to regard the π_z^***2p** component of the bond in terms of the overlapping of hybrid orbitals, *i.e.* using the valence bond theory, and the π component in terms of the molecular orbital theory. Let us consider the bonding in the C_2H_6 molecule. The structure of the ethylene molecule is flat with the three bond angles at each carbon atom being approximately 120°. Since each carbon atom is attached to three other atoms (two hydrogen atoms and one carbon atom), we need invoke only three orbitals of the carbon atom for σ bonding. In accordance with the structure of the molecule, these orbitals will be $\mathbf{sp}^2$ hybrid orbitals derived from **2s** and two of the **2p** orbitals:



Two of the $\mathbf{sp}^2$ hybrid orbitals overlap with the **1s** orbitals of two hydrogen atoms producing two C – H σ bonds; the third $\mathbf{sp}^2$ orbital overlaps with the corresponding orbital of the second carbon atom giving rise to a C – C σ bonds (Figure 1.22*a*). If we assume that the $\mathbf{sp}^2$ orbitals are derived from the $\mathbf{2p_x}$ and $\mathbf{2p_y}$ orbitals, then the σ bonds lie in the *xy* plane with the unhybridised $\mathbf{2p_2}$ orbital at right-angles to it.



This arrangement is shown in Figure 1.22*b*. The close proximity of the carbon atoms results in the overlapping of the $\mathbf{p_x}$ orbitals, and in terms of the molecular orbital theory, a bonding π orbital and an antibonding π orbital are formed. Each $\mathbf{p_2}$ orbital originally contained one electron, and these, now paired, occupy the bonding π orbital. Bonding of two carbon atoms is thus due to two pairs of electrons, one pair in the σ orbital and the other in the π orbital. The two lobes of the π orbital prevent rotation about the carbon-carbon axis. Description of the triple bonding in acetylene is similar, except that **sp** hybridisation is assumed to account for the linear structure of the molecule, the $\mathbf{p_y}$ and $\mathbf{p_x}$ orbitals of one carbon atom overlap sideways with the corresponding orbitals of the

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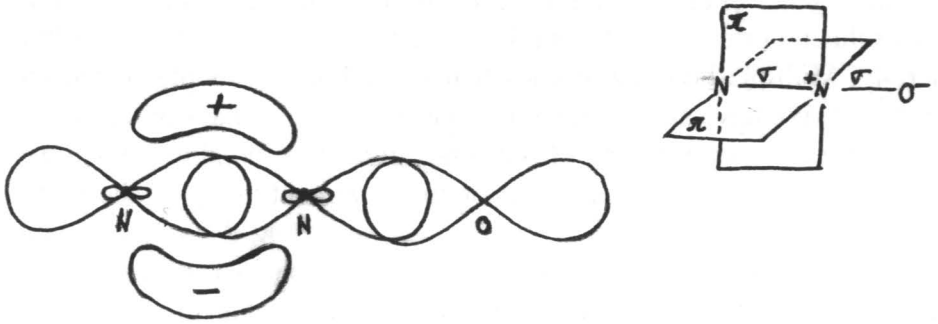
other carbon atom so that the C – C σ bond is supplemented by two π bonds. For elements in the second period and beyond, the **d** orbitals available are frequently utilized for multiple bonding.

Let us consider the bonding in nitrous oxide. The linear structure of the NNO molecule can be accounted for by assuming that the central nitrogen atom is **sp** hybridised:



In the 1869 version of the periodic law set forth by Mendelejev, it stated that "the properties of simple bodies as well as the forms and properties of compounds of elements are in a periodic relationship with the atomic weights of the latter". As is well known, Mendelejev's law was and still is of "predictive" value. Two years later, in 1871, Mendelejev described in greater detail elements yet to be discovered, which were analogues of boron, aluminium, and silicon. We named them "ekaboron", "eka-aluminium" and "ekasilicon". The prefix "eka" was borrowed from the Sanskritt language in which it means "one". Thus, "ekasilicon" stands for the first analogue of silicon (analogue number one), and so on. In these memoirs, Mendelejev wrote that prediction of properties of elements is an extension of the periodic law, and that he attempted this in order"to perpetuate the periodicity of the elements". In these words, it was a risk but a judicious and successful one.

Mendelejev predicted gallium (Ga = eka-aluminium), scandium (Sc = ekaboron), and germanium (Ge = ekasilicon) but also analogues of cesium (Fr, francium), barium (Ra, radium), tantalum (Pa, protactinium), and other elements, still unknown at the time. The predictions concerning Ga, Ge, and Sc came true within a relatively short period of time. Lecoq de Boisbaudran (France) discovered gallium in 1875, Nilson (Sweden) discovered scandium in 1879, and Winkler (Germany) discovered germanium in 1881.

The periodic law has played a key role in the discovery of other elements, such as hafnium, rhenium, and protactinium (all discovered in the 20^{th} century); the search for these elements was based on the chemical analogy suggested by the periodic law. The periodic law has also been instrumental for identifying artificially synthesized elements.

Mendelejev's discovery has received universal acclaim. The American physicists and chemists who discovered element 101 (Ghiorso, Harvey et al.) named it "mendelevium" in 1955. They wrote that this was done in recognition of the leading role of the great Russian chemist Dmitry Mendelejev, who was the first to use the periodic law for predicting the properties of elements yet to be discovered and, in particular, to provide a key for discovering transuranium elements also known as actinides.

In 1969, chemists throughout the world observed the centenary of the periodic law. Glenn Seaborg, who must be credited for discovery and identification of many tranuranium elements, figured prominently at the centennial celebrations. He took part at the ceremony held at UNESCO in Paris in March, 1969, and at the Mendelejev symposium sponsored by the American Chemical Society in April of the same year. Then, Seaborg spoke at the congress held in Leningrad to Mark the centenary of the periodic law and, finally, chaired the symposium in honor of Mendelejev's discovery, convened in Houston, Texas (USA), in November, 1969. The famous American scientist, who supervised the effects leading to synthesis of most currently known transuranium elements, wrote that in this previous papers presented at other scientific meetings devoted to evolution of the periodic system, he emphasized the fact that the elegant simplicity of Mendelejev's periodic table

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had prompted physicists and chemists to continue their search for interrelationships between the chemical properties of the elements.

Luminaries of modern science acknowledge the undiminishable importance of Mendelejev's discovery and express their admiration for the genius of our compatriot. However, many histories of chemistry abroad contend that the discovery of the periodic law should be credited not only to Mendelejev but also to the German chemist Lothar Meyer who had "simultaneously and independently" arrived at the principles underlying the periodic law.

In fact, the course of events was as follows. Mendelejev announced his discovery of the periodic law on March 1, 1869, at the 2nd Congress of Russian Natural Scientists and Doctors; at the same time, he wrote a paper about the periodic law and submitted it for publication. In 1870, Meyer had a paper on the name subject published in "Liebig's Annals" (the paper was sent in December, 1869). In this paper (1870), Meyer made reference to Mendelejev's paper which he knew from an abstract and indicated that the table be proposed was substantially identical with the one presented by Mendelejev

Meyer had never come up with the idea of periodicity before he heard about Mendelejev's paper. A case in point his previously published paper (1864) in which not a word was said about the regularities found by Mendelejev, not was anything said about the dependence of any properties of the elements on their atomic weight.

The prominent Russian chemist, L.A. Chugaev wrote that, before publication of Mendelejev's paper, the idea of periodic changes in the properties of the elements arranged according to their atomic weights never occurred to Meyer who borrowed it from Mendelejev. It was only after Mendelejev presented his paper that Meyer proposed his well-known curve showing atomic volumes of the elements versus their atomic weights. Before Mendelejev's paper, Meyer merely grouped elements according to their valence and the difference between atomic weights in different series. As regards Mendelejev himself, this is what he wrote about the priority in the discovery of what he termed as "periodic law': "Insofar as studies of Prof. Lathar Meyer into the periodic law are concerned, judging from the manner itself in which his first paper is written (Lieb. Ann. Supp., VII, p.357 (1870)) - the paper beginning with reference to the abstract of my above/mentioned work dated 1869 - it is obvious that he adopted the periodic law in the precise from I proposed it". Mendelejev's priority in the discovery of the periodic law is beyond any reasonable, doubt, and it has recognized by all those who are familiar with the history of the periodic law. The periodic law discovered by Mendelejev, while remaining invariable in principle, is being evolved and improved as our knowledge about the nature of matter expands and is revised. At the turn of this century, the science of matter made a tremendous leap forward with the elaboration of the nuclear theory of atomic structure and also experimental measurements of charges of atomic nuclei and electrons (Mosely, Thomson, Rutherford, Bhor et al., 1911-1914). It was found that the atomic nucleus coincides with the ordinal number of the element in the periodic system. If the atom of an element is in an electroneutral state, the atomic nucleus with a positive charge Z is surrounded by the same number Z of electrons, each carrying a unit charge. Since it became clear that it is the nuclear charge that makes each element unique and the atomic weight of an element is a quantity dependent on the nuclear charge, the statement of the periodic law has been revised and is currently as follows: **The physical and chemical properties of elementary substances as well as the forms and properties of compounds are a periodic function of the nuclear charge (or, which is practically the same, of the atomic numbers of elements)**. This restatement of the law does not mean than the latter in its original form is no more valid and can be discarded. Indeed, there is a certain relationship between the atomic weight and number (or nuclear charge): atomic weight A is almost twice the atomic number ($A : Z \approx 2$). For many elements at the beginning of the periodic system (from He to O) this ratio equals two exactly, then it increases from 2.1 (Fe) to 2.5 (Hg) and 2.6 (U). The increase in the number of protons in the nuclei of heavy atoms calls for an increase in neutrons so that nucleus does not disintegrate because of repulsion of the protons "undiluted" with an appropriate number of neutrons. Yet this ratio, which is dependent on the ratio between protons and neutrons in the atomic nucleus, approaches two and remains virtually

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constant for all elements of the periodic system. Hence, atomic weight A and nuclear charge Z are proportional quantities. Consequently, Mendelejev did make any mistake when he took the atomic weight as the basic characteristic of an element. It is known that this quantity is directly related to the magnitude of the nuclear charge and that responsible for periodic changes in the chemical properties of the elements are those in the electron shell structure of atoms. Mendelejev made a great discovery when nothing definite was known about the atomic structure. It took quite a great deal of foresight and intuition of a genius to formulate the periodic law at that time. Mendelejev himself could not explain the periodicity of changes in the chemical properties of the elements. As he wrote in one of his works: " It (the periodic law) is now emerging as a new, only partially solved profound mystery of nature, which allows us comprehend the laws but gives a very remote chance to gain a full insight into the true essence of these laws". Mendelejev was fully aware of the enormous scientific potential of his discovery, and he was proud indeed that the priority in the discovery was his and, primarily, of the Russian science. ... The wide applicability of the periodic law with a lack of understanding of its underlying principles is another indication of its utmost novelty and deep penetration into the nature of chemical phenomena, and O, a Russian, am proud for my contribution to formulation of this law".

The kind of MO are illustrated in Figure 30

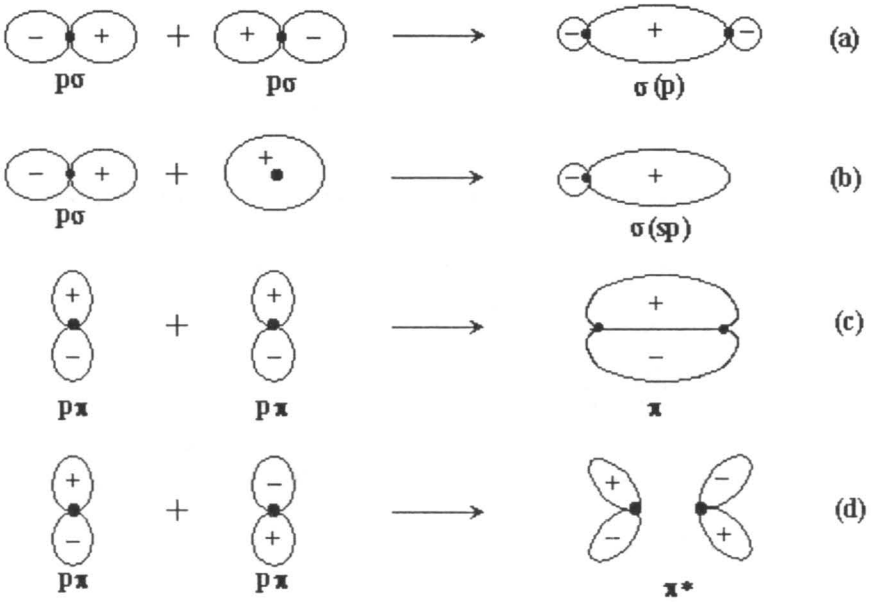

Figure 30 - Diagrams illustrating the formation of some simple tw-center MO's from atomic orbitals

σ (sigma) MO has a cylindrical symmetry about the internuclear axis. A π-type orbital is one whose nodal plane includes the molecular oxis.

We may begin by treating the three types of orbitals **s**, $\mathbf{p}_\sigma$ and $\mathbf{p}_\pi$ entirely separately. Thus the **s** orbitals give rise to σ_s and σ_s^*, bonding and antibonding MO's, respectively. The two $\mathbf{p}_\sigma$ orbitals combine to give σ_p and σ_p^* MO's. The $\mathbf{p}_x$ and $\mathbf{p}_y$ orbitals on each atom are of the same energy and form two π-type bonding MO and two π^*-type antibonding MO. The two MO's of each pair are said to be degenerate.It is found that the magnitudes of the three sorts of overlaps decrease in the order S-S ≈ p_σ - p_σ > p_π - p_π, and the corresponding values of β should also decrease in the same order. On the basis of these considerations for the elements of the first short period the **p** orbitals have higher energies than the **s** orbitals, the energy level diagram shown in Figure 31*a* can be drawn. However, this diagram ignores one factor in the problem and is therefore not entirely correct. We have assumed that the **s** orbitals interact only with one another and the $\mathbf{p}_\sigma$ orbitals only with one

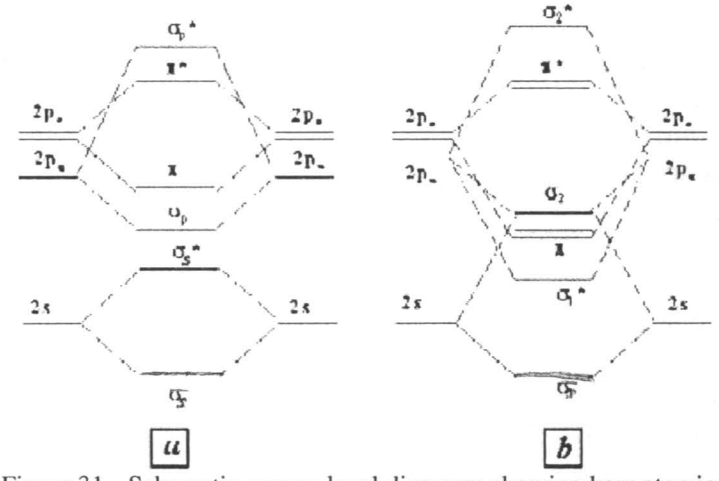

Figure 31 - Schematic energy level diagrams showing how atomic orbitals of two (identical) atoms of the first short period to form molecular orbitals

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another. It is wrong to neglect entirely the other interactions permitted by symmetry. Actually there are interactions between **s** and $\mathbf{p}_\sigma$ orbitals (see Figure 31*b*). As a result of the mixing of **s** and **p** character in all the σ MO's, their energies are shifted such that the lower two become more stable while the upper two become less stable.

Now, referring to Figure 31*a* we see that if these shifts are sufficiently large, there may be a charge in the qualitative order of the levels, namely, the 3-rd lowest orbital may be a π orbital instead of a σ orbital as shown in Figure 31*b*. The extent of the energy shifts will be greatest when the energy difference between the s and p orbitals is least because then they can interact most. The **s - p** energy difference is relatively small for Li (≈ 2 eV) and increases steadily until it is about 27 eV for Ne. Thus, while we might definitely expect the pattern shown in Figure 31*b* at the beginning of the period, the pattern in Figure 31*a* a might be correct at the end (i.e. for F_2). On the basis of experimental data, the pattern in Figure 31*b* does appear to persist as for, at least, as N_2.

We shall now consider the electron configurations of each of the homonuclear diatomic molecules of the elements in the first short period on the basis of the LCAO-MO theory outlined above.

Li_2 $(\sigma_1)^2$ the bond order (B.O) $= \frac{2}{2} = 1$

diamagnetic molecule

Li — Li 2.67 A° and H — H 0.74 A°

$E_{Li—Li}$ 25 kcal/mol; $E_{H—H}$ 103 kcal/mol.

Two factors account for these differences. First, the **2s** and **2p** orbitals of Li are much larger and more diffuse than the **1s** orbital of hydrogen. Thus they tend to overlap less effectively and with maximum overlap at a greater internuclear distance than in the case of the hydrogen 1s orbitals. Second, the electrons occupying the **1s** shells of the Li atoms cause a repulsion between the atoms.

Be_2 $(\sigma_1)^2 (\sigma_1^*)^2$ B.O $= \frac{2-2}{2} = 0$ Be_2 has not been observed

B_2 $(\sigma_1)^2 (\sigma_1^*)^2 (\pi)^2$ on the basis of Figure 31*b*

$(\sigma_1)^2 (\sigma_1^*)^2 (\sigma_2)^2$ on the basis of Figure 31*a*

Experiment shows that B_2 has two unpaired electrons in a π orbital; thus Figure 31*b* is still correct at B_2.

B.O. $= \frac{4-2}{2} = 1$ (one net π bond, since the σ interactions cancel).

C_2 For this molecule the level order in Figure 31*b* predicts a configuration $(\sigma_1)^2 (\sigma_1^*)^2 (\pi)^4$, while that the event that the σ_2 and π levels are very close, a $(\sigma_1)^2 (\sigma_1^*)^2 (\sigma_2)^1 (\pi)^3$ configuration is also possible.

The latest experimental results indicate that the ground state is derived from $(\sigma_1)^2 (\sigma_1^*)^2 (\pi)^4$ configuration although a state derived from the $(\sigma_1)^2 (\sigma_1^*)^2 (\sigma_2)^1 (\pi)^3$ configuration lies only ≈ 610 cm^{-1} higher. B.O = 2 is in according to bond energy of 150 kcal/mol.

N_2 For N_2, with a very high bond energy (225 kcal/mol) and no unpaired electrons, either of the configurations $(\sigma_1)^2 (\sigma_1^*)^2 (\pi)^4 (\sigma_2)^2$ or $(\sigma_1)^2 (\sigma_1^*)^2 (\sigma_2)^2 (\pi)^4$ would be acceptable, each giving a B.O = 3. That the former is actually correct by the fact that the odd electron in N_2^+ is in a sigma orbital according to spectroscopic evidence.

O_2 For this molecule the electron configuration might be either $(\sigma_1)^2 (\sigma_1^*)^2 (\sigma_2)^1 (\pi)^4 (\pi^*)^2$ or $(\sigma_1)^2 (\sigma_1^*)^2 (\pi)^4 (\sigma_2)^2 (\pi^*)^2$ .B.O.= 2 and two unpaired electrons are expected. Both these predictions are in good accord with experiment, the experimental bond energy being 118 kcal/mol. It is also interesting to note that the addition of electrons

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to O_2 causes the bond length to increase (d_{O2}=1.21 A°; d_{O2^-} = 1.26 A°; $d_{O2^{2-}}$ = 1.49 A°) while the loss of an electron causes the bond to shorten (d_{O2^+} = 1.12 A°).
These results are therefore in excellent accord with the MO electron configuration, since the orbital to or from which electrons are added or removed is an anti-bonding one. In O_2^+ B.O. = 2.5 and in O_2^{2-} B.O. = 1.

F_2 On adding two more electrons to the O_2 configuration we fill all orbitals except σ_2^* B.O. = 1.

FURTHER PROPERTIES OF ATOMS, MOLECULES AND CHEMICAL BONDS

1. Bond Energies

For a diatomic molecule the bond energy, **D**, is equal to the enthalpy of the reaction

$$XY_{(g)} = X_{(g)} + Y_{(g)} \quad \Delta H = D$$

where the molecule and the atoms are all in their ground states. The bond energy is a function of temperature, and the best value to use would be that for the hypotheoretical reaction at O^0K. An Ab_n type molecule where all B's are equivalently bonded to A (i.e. BF_3) all B-F bond energies, $D_{B\text{-}F}$, must be equal and the relation:

$$BF_{3\,(g)} = B_{(g)} + 3\,F_{(g)} \qquad \Delta H = 3\,D_{B\text{-}F}$$

is obvious. Thus if we know the heats of formation of $BF_{3\,(g)}$, $B_{(g)}$ and $F_{(g)}$ we can readily calculate $D_{B\text{-}F}$. This vaqlue is called the mean thermochemical bond energy. However, it is not the energy, ΔH_1, of the process.

$$BF_{3\,(g)} = BF_{2\,(g)} + F_{(g)} \qquad \Delta H_1$$

since when the first bond is broken, the nature of the remaining two will necessarily be altered to some extent. Also ΔH_2 and ΔH_3

$$BF_{2\,(g)} = BF_{(g)} + F_{(g)} \qquad \Delta H_2$$

$$BF_{(g)} = B_{(g)} + F_{(g)} \qquad \Delta H_3$$

are not likely to be equal to one another, or to ΔH_1. It is of course, true that

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = 3\,D_{B\text{-}F}$$

because the Hess'law can be applied.

There are many molecules in which two or more different kinds of bonds exist. In C_2H_6 for example:

$$C_2H_6 = 2\,C_{(g)} + 6\,H_{(g)} \qquad \Delta H = 6\,D_{C\text{-}H} + D_{C\text{-}C}$$

we must know one of the two unknowns $D_{C\text{-}C}$ or $D_{C\text{-}H}$. We may evaluate a mean C-H bond energy in methane since there are enough experimental data to tell us the energy of the process:

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$$CH_{4\,(g)} = C_{(g)} + 4\,H_{(g)} \qquad \frac{1}{4}\,\Delta H = D_{C\text{-}H}$$

2. Electronegativities

The original qualitative definition of Pauling is: " Electronegativity is the power of an atom in a molecule to attract electrons to it self."

It is not, however, the same as electron affinity, as will be seen. Suppose we consider a bond A-B between dissimilar atoms A and B. From The viewpoint of V.B. theory this will be a resonance hybrid

$$\underset{(a)}{A\text{—}B} \quad \leftrightarrow \quad \underset{(b)}{A^- B^+} \quad \leftrightarrow \quad \underset{(c)}{A^+ B^-}$$

Pauling established a scale of electro-negativities based on " excess " bond energies. The energynof the bond, D(A-B), is the sum of a nonpolar contribution, D_{np} (A-B), and a polar contribution, D_p (A-B). The nonpolar contribution is the energy expected from the mean of the nonpolar bond energies D(A-A) and D(B-B). The polar contribution, designated Δ, is a measure of the bond's expected polarity, which results from a displacement of the electronic charge toward one atom. Ordinarily, the polarity of the bond increases with increasing differences in electro-negativities of A and B.

$$D(A - B) = D_{np}\,(A - B) + \Delta_p\,(A - B)$$

$$D_{np}(A - B) = \frac{D_{np}(A - A) + D_{np}(b - B)}{2}$$

$$D_p(A - B) = \Delta = D\,(A - B) - \frac{D_{np}(A - A) + D_{np}(B - B)}{2}$$

The negative values can be avoided by using the geometric mean of the bond energies ($\sqrt{D(A - A) \times D(B - B)}$) to give Δ' values.

$$\Delta' = D\,(A - B) - \sqrt{D(A - A) \times D(B - B)}$$

Note that in each case D(A - B) is greater than the geometric mean of D(A - A) and D(B - B). This mean energy is taken as the (hypothetical) A - B bond energy if the A - B bond were purely covalent, that is, represented only by canonical form (a). The differences, Δ's, are identified as "ionic resonance energies" due to resonance of (a) with (b). It is assumed that the greater the electro-negativity differences the more ionic resonance there will be, and hence the larger will be the value of Δ. However, Δ is not proportional to the electro-negativity differences $x_A - x_B$. Thus

$$(x_F - x_{Si}) - (x_{Br} - x_{Si}) = (x_F - x_{Br})$$

but $$89 \quad - \quad 25 \quad \neq \quad 16$$

In general the quantities $\Delta^{1/2}$ do seen to be additive or approximately so. In the present case

$$9.3 \; - 5.0 \; = 4.3 \approx 4.0$$

Pauling set up a table of relative electronegativityes using the relation

$$x_A \; - x_B = K \times \Delta^{1/2}$$

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The constant K was taken as $23^{-1/2}$ (Δ's were expressed in eV). Among the dozens of other methods proposed for estimating experimentally or calculating electro-negativity values, we shall mention only two.

Mulliken showed by theoretical arguments that the tendency of an atom in a molecule to complete with another atom to which it is bound in attracting the shared electrons should be proportional to (J + A) /2, that is to overage of its ionization potential and its electron affinity. It is found that when J an A values are expressed in electron volts the hulliken electro-negativity values can be adjusted to give the least mean deviation from Pauling's by dividing then by 3.15.

The empirical method of Allred and Rochow seems to have certain advantages stemming precisely from its complete and strict empiricism. An electron in a bond is assumed to be attracted by one of two nuclei according to Coulomb's law.

$$\text{Force} = \frac{Z^* e^2}{r^2}$$

where Z^* is the effective nuclear charge which the electron feels and r is its mean distance from the nucleus.

Z^* is estimated using the Slater's method, and r is taken as the covalent radius of the atom, which for a homonuclear diatomic molecule is half the internuclear distance.

Equation Allred and Rochow's electro-negativities is obtained:

$$x_{AR} = 0.359 \frac{Z^*}{r^2} + 0.744$$

The electro-negativity of an element is dependent of its valence (i.e. for S in SCl_2 has a different electro-negativity from S in SF_6).

3. Bond Lengths and Covalent Radii

The lengths of bonds, are the intermolecular distances in molecules. If we consider a homonuclear diatomic molecule with a single bond; such as F_2 or Cl_2, we can assign to the atoms F and Cl covalent single bond radii equal to one-half of the internuclear distances in the respective molecules.

The covalent radius of the chlorine atom is one half of the chlorine-chlorine distance. The elements which form molecules with many bonds other methods of estimating the radii are used. For example, the triple bond radii of carbon and nitrogen can be calculated for the bond lengths in HC≡CH and N≡N, as 0.60 and 0.55, giving 1.15 for −C≡N as compared to experimental values of ≈ 1.16. The higher the order of a bond between two atoms, the shorter it is (i.e. C–C 1.54; C=C 1.33; C≡C 1.21).

The C–C distance in diamond is found to be 1.54 ± 0.01 A°, so the covalent radius of C is taken as 1.54/2 = 0.77.

In the molecules where there are bonds between atoms of disparate electro-negativities the bond length can be calculated by the Schomaker-Stevenson equation

$$r_{A-B} = r_A + r_B - 0.09 \mid x_A - x_B \mid$$

This relationship is not very satisfactory because in some molecules there are possibilities of double bonding. For example in the case of BF_3 the bond shortening can also be attributed to B–F double bonding since boron has a vacant p_z orbital and the fluorine atoms have a filled p_z orbitals.

It is probable that both ionic-covalent resonance and multiple bonding contribute significantly.

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4. Bond and Molecular Polarity

The electrical polarity of a molecule is expressed as its dipole moment. A system consisting of a positive charge, + x, and a negative charge, - x, separated by a distance, d, possesses a dipole moment of a magnitude xd. If x is equal to the electronic charge (4.80×10^{-10} e.s.u) and d is $1^{\circ\circ}$ A°, xd = 4.80 D (Debye) units. The dipole moment is a vector quantity since it has a definite direction as well as magnitude.

The electronic structure of Hcl can be expressed in a very simple way by writing it as an ionic-covalent resonance hybrid of two Lewis structures:

(a) (b)

we may use equation for the total wave function of MO:

$$\Psi_{tot} = \left(1 - 2\lambda + 2\lambda^2\right)^{-1/2}\left[(1-\lambda)\,\Psi_{cov} + \lambda\,\Psi_{ion}\right]$$

and define the percent ionic character as 100 λ. The internuclear distance in Hcl is 1.27 A°. If λ were unity, the dipole moment would be 6.1 D.

$$\mu = x \times d = 1.27 \times 4.80 = 6.1 \text{ D}$$

μ represents the expected dipole moment for 100% ionic Hcl. The percentage of ionic character is obtained from the ratio of the observed dipole moment to the dipole moment for complete electron transfer.

The observed dipole moment for HCl is 1.03 D (1.03/6.1 - 17% i.e., λ = 0.17).

By plotting the various percentages obtained against x_X - x_H, where x_X is the electronegativity of the halogen atom, he obtained a smooth curve given by the equation

$$i\% = 18(x_X - x_H)^{1.4}$$

The main source of error is the assumption that Ψ_{cov} is nonpolar.

4.1. Polar nature of a heteronuclear bond

The HCl molecule is a neutral system. If we place the centroid of charge of these two bonding electrons exactly half way between the nuclei, the system will have no dipole moment. However, since the hydrogen orbital is much smaller than the chlorine orbital, thecentroid of charge for the bonding electrons must be closer to H than to Cl and a dipole will result, namely,

$$\overline{\text{H - Cl}}.$$

4.2. Orbital moments of unshared electrons

In the HCl molecule the chlorine atom has three pairs of electrons, which have an orbital dipole moment vector of magnitude V pointing along the axis of the orbital. If the three pairs of electrons lie in the three equivalent hybrid orbitals, and the bond direction lie on the Z axis, the total dipole moment contribution in the bond direction is - 3V cos 71^0, namely,

$$\frac{-3\,V\cos 71^0}{H - Cl}$$

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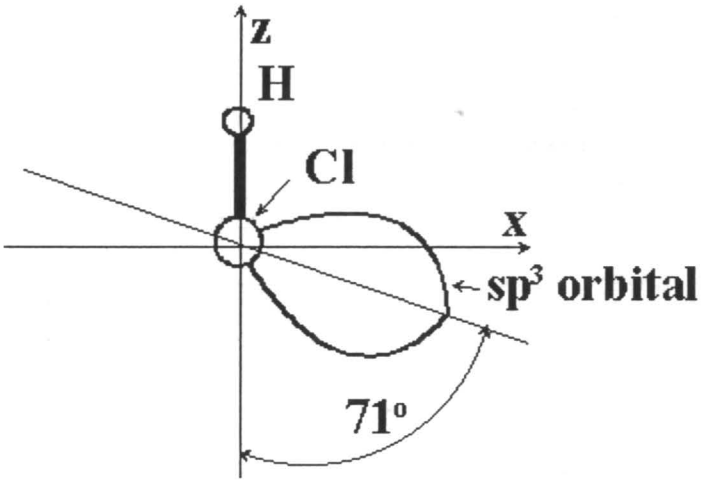

The dipole moment of a polyatomic molecule can be considered to be the vector sum of various contributing dipols. Suppose we have a regular pyramidal molecule, AB_3. Because of its symmetry its dipole moment must lie along the three-fold axis of symmetry. If each A-B bond axis makes an angle, θ, with this symmetry axis, we might say the net molecular dipole moment, μ, is the vector sum of three equal bond moments, each of magnitude $(\mu/3)\cos\theta$.

Unfortunately, this picture is unsatisfactory. The dipole moments of the pyramidal molecules NH_3 and NF_3 of 1.5 and 0.2 D respectively cannot be explained only if we consider the influences to the dipole moment both of the bond moments and orbital moments of unshared pairs of electrons. In Figure 32 we shown the dipole moments of NH_3 and NF_3.

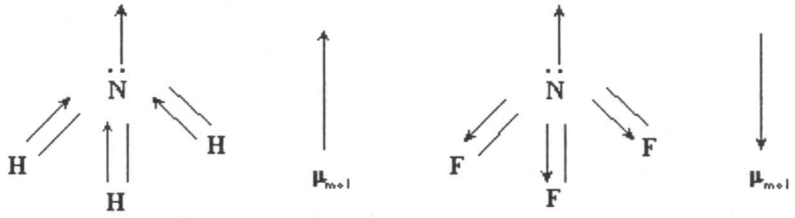

Figure 32 - Diagram illustrating how the molecular dipole moment, μ_{mol}, can be regarded as a vector sum, of bond moments and the lone pair moment in NH_3 and NF_3

It is possible that the orbitals are not directed exactly along the internuclear lines. That is, the bonds may be a little bent.

5. Some Relations between Bond Properties

A bond property whose magnitude is directly related to the bond order is the force constant of the bond. The force constant of a bond between atoms A and B is given by equation.

$$\nu(\text{cm}^{-1}) = \frac{1}{c}\sqrt{\frac{f}{4\pi^2\mu}}$$

ν is the vibration frequency of the bond expressed in wave numbers (cm^{-1}), observed in IR or Raman spectrum

c is velocity of light

μ is the reduced mass of the A-B oscillator in grams

Specifically, we have the following relationships.

(1) As bond order increases:
- length decreases
- energy increases
- force constant increases

(2) As bond length increases:
- energy decreases
- force constant decreases

(3) As energy increases:
- length decreases
- force constant increases

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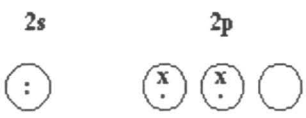
(4) As force constant increases:
length decreases
energy increases
None of these relations is linear.

Repulsive force is proportional to $\frac{1}{l^{10-12}}$,

l is the bond length.

6. Coordinative Covalence or Dative Bonding

Carbon monoxide provides a common case of molecule formation in which an s electron of carbon is not promoted. Here we would expect carbon to have achieved the configuration and oxygen to have an $s^2 p^6$ configuration.



However, the high dissociation energy of CO and the very short C-O bond distance suggest that the Lewis structure is better represented by

$^{(-)}$:C ≡ O:$^{(+)}$ or simply :C ≡ O:

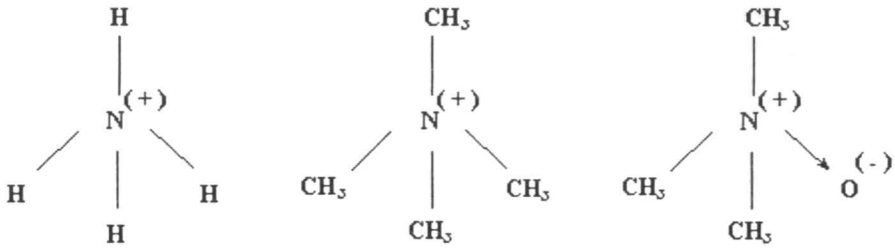
The arrow in the right-hand formula is a convention sometimes used to indicate that oxygen donated both of the electrons in the bond. This so-called coordinate covalent bond, or dative bond cannot be distinguished from an ordinary covalent bond once it is formed.

The charges shown, called formal charges, and these may be calculated by assigning half of the electrons shared between two atoms to each atom and calculating the resulting charge on the quasi ion.

The sum of the formal charges in a molecule will be zero.

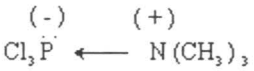
Formal charges are assigned assuming 100% covalent character, whereas oxidation number assignments assume no electron sharing.

Nitrogen can form dative bonds as follows.

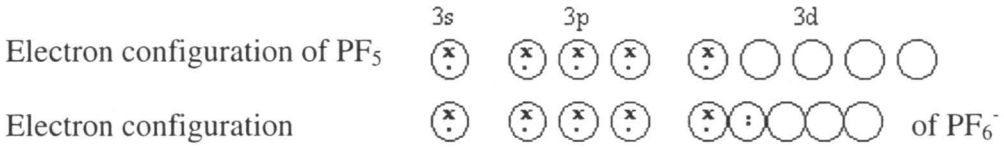


An arrow may be used for the N→ O bond, since it can be identified as the dative bond. Arrow are not appropriate for NH_4^+ or $N^+(CH_3)_4$, because the four bonds are equivalent. Phosphorus can donate its unshared pair in dative bonding, as in

or it can accept a pair of electrons into ad orbital as in



Phosphorus in PF_5 can add a fluoride ion by accepting a pair of electrons into one of its empty **d** orbitals, as shown below.



Through dive bonding, phosphorus can form four and six bonds, as well as the usual compounds such as PX_3 and PX_5. This series may be illustrated by the following species.

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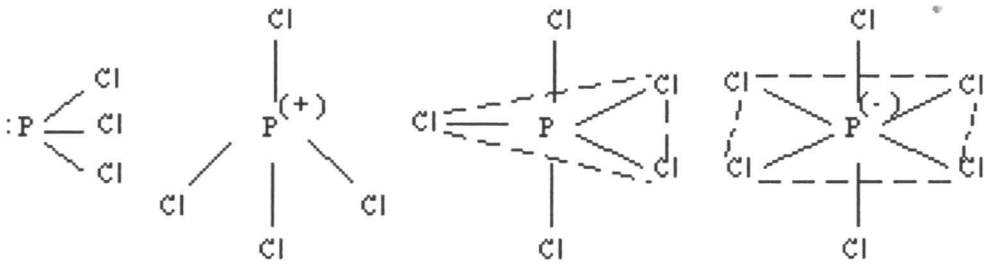
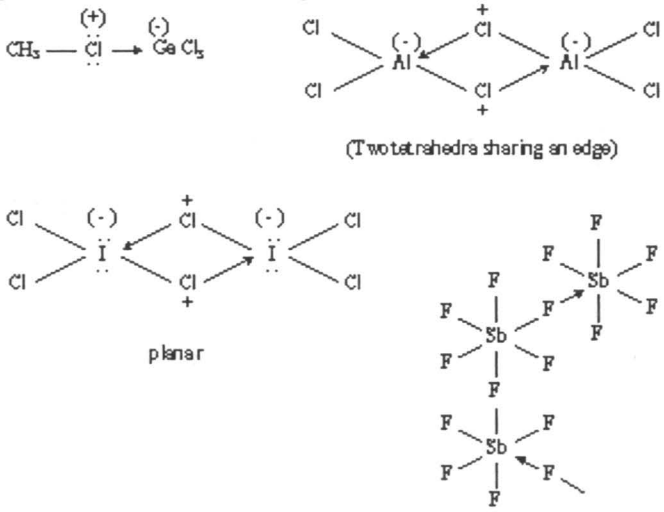
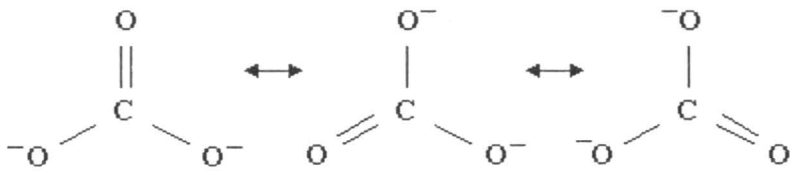


In addition to the compounds XX', XX'_3, XX'_5, XX'_7 for the heavier halogens, dative bonding allows the formation of ICl_2^-, ICl_4^-, and IF_6^-. Halogens can also form two bridging bonds, as shown in Figure 33.



7. Resonance

Some molecules or ions cannot be represented adequately by a single valence bond formula. Pauling introduced the concept of resonance to adopt the simple valence bond notation to situations in which electrons are delocalized. Three structures are written for the carbonate:



(a) (b) (c)

Do not interpret the three contributing structures as having any independent existence. There isn't an equilibrium among the three structures. The assignment of a bond order of 1 1/3 to the C–O bond in carbonates is straight forward, since the three most resonable contributing structures are equivalent. For example, the sulfate ion, may be viewed as arising from dative bonding between a sulfide ion and four oxygen atoms (a), or from the sharing of two pairs of electrons between each oxygen are sulfur (b). In addition to these extenes, we may write the intermediate structures (c); The actual structure of the sulfate ion would be are overage of all the structures shown, weighted according to the number of equivalent structures and their relative energies.

It has been estimated that the bond order in sulfates is approximately 1.5, corresponding most closely to (d).

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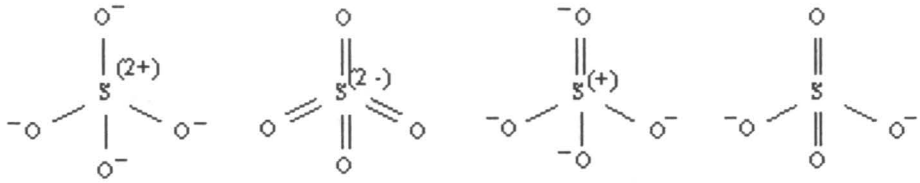


(a) (b) (c) (d)

The familiar application of resonance to benzene includes, the usual Kekulé structures (a and b)

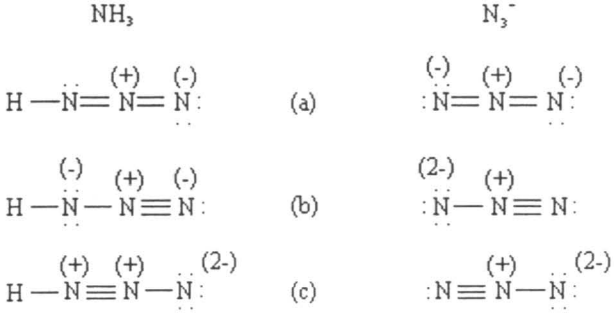
(a) (b)

The elimination of unlikely structures and the selection of the more important contributing structures, is facilitated by the following rules.

1. The contributing structures should have the same or nearly the same atomic positions. The closer the bond angles and the lengths of a contributing structure are to those of the actual molecule, the greater the " contributions " of that structure to the hybrid.

(c) (d) (c) and (d) are less important

2. All contributing structures of a particular molecule must have the same number of un paired electrons.
3. Contributing structures should not differ too widely in the positions of electrons or not differ greatly in energy. This rule also eliminates structures in which there are more than eight electrons around an atom.
4. Like charges should not reside on atoms close together in a contributing structure. In NH_3, structure (c) is relatively un important, because of the (+) charges on adjacent N atoms and also because of the double negative charge on the remaining N atom.



Since the similar structure for the N_3^- ion does not give (+) charges on adjacent N atoms, it should be more important than for the molecular acid. The change in the relative importance of the last contributing structure should result in the same bond order (about 2) for each bond in N_3^-, but in a bond order less than 2 for the N– N bond nearer the H atom and a bond order greater than 2 for the terminal N– N bond in HN_3. In N_3^- there is a resonance stabilization of the anion.

5. Contributing structures in which negative charge resides on an electronegative element and positive charge resides on an electropositive element are more important than those in which the reserve is true. For HF the contributing structure $H^{(+)}$ $F^{(-)}$ is an important one: the ionic structure $H^{(+)}$ $F^{(-)}$ is not.

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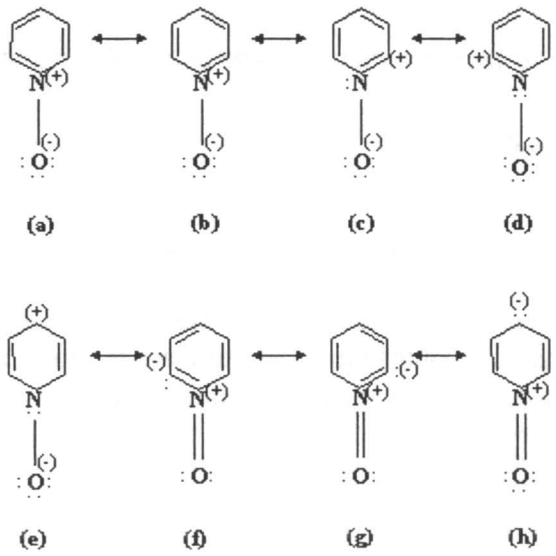
6. The greater the number of covalent bonds, the greater the importance of a contributing structure. In the case of pyridine-N-oxide, structures (c-e) have a favorable distribution of charges from the standpoint of the electro-negativity of the atoms involved, but the fact that these structures contain one less bond than the (a and b) structures diminishes their importance.

Rule 5 indicates that structures (f-h) should be even less important than (a) and (b), because the (+) charge is on the more electronegative nitrogen and the (-) charge is on a carbon atom.



The discrepancy between calculated and observed heats of formation is called the resonance energy. Typical resonance energies (KJ/mole) are benyene, 155; naphthalene, 314; C≡O, 439; and O=C=O, 151; The increased stability of molecules stabilized by resonance is reflected in the shortening of bond lengths compared to the overage expected from the contributing structures.

The greater the number of contributing structure the greater the delocalization of electronic charge and hence the more stable the molecular delocalization of charge on an atom is usually an unstable situation. The increasing acidity in the series HCl O, $HCLO_2$, $HClO_3$, $HClO_4$ is determined largely by the greater stability of the anions containing several oxygen atoms, because of the greater delocalization of the negative charge. For the most part, the negative charge in ClO^- must reside on the oxygen atom. In ClO_4^- the negative charge is spread over four equivalent oxygen atoms.

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INTERMOLECULR BONDS.
BONDINGS THROUGH van der WAALS FORCES

The interatomic bonds in a molecule are realized by the superposition of atomic orbitals in molecular orbitals that spreads over all component atoms of the molecule, are very strong bonds. The covalence would not modify through the chance of state of the substance and after the molecular substances dissolves into a solvent.

Unlike the covalences the bonds that settles between the molecules of the substances in different states are very weak. They are evidenced by the following phenomenon:

-The deviations of the rare gases from the ideal gasses laws: van der Waals purposed the existence of some attractive forces between the molecules of the gasses and that acts in the same sense as the pressure:

$$(p + \frac{a}{V^2})(V - b) = nRT$$

- The Joule-Thomson Effect: the relaxation of a strong comprimated gas by flowing through a narrow orifice determines a cooling of the gas.
- The solidification of the gases, including the rare ones (He or Ne), those are incapable of forming bonds of normal valences. These attractive forces between the molecule are known as van deer Walls forces . They are actually electrostatic forces too, but they don't manifest between separate and opposite electric charges of the ions , but between the electric dipoles.

Van deer Waals forces have two principal characteristics:

- They are weak in comparison with the covalences because they vary inverse proportional with the seventh power of the distance r, between the molecules
- They cannot be saturated because, like the electrostatic forces they behave uniformly around the molecule, acting on smaller distances

The attractive interactions van deer Waals are of three kinds: dispersion interactions (London), of orientation and of induction.

1.The van deer Waals dispersion forces act between all types of molecules, at the nonpolar molecules being the only type of attractive forces between the molecules. The nature of this forces was given by London (1930) in the base of the quantum mechanics theory, fact that determines the meaning of London forces. These interactions are also known as dispersion forces, because they are conditioned by the polarizability of the molecule as the dispersion of light through hollow medium.

The scattering forces are formed even in the perfect symmetric molecules, because the molecule can be considered an harmonic oscillator, because the nucleus may vibrate contrarily with the electrons, determining the formation of temporary dipole momentum. The temporary dipole can determine into a neighboring molecule of a induced dipolar momentum, both moments being attracted.

It was demonstrated that the interaction energy of the two moments is different from zero.

$$Ed = -\frac{3\alpha_1\alpha_2}{2r^6} \cdot \frac{I_1 I_2}{I_1 + I_2}$$

were α_1 and α_2 are the polarizability coefficients; I_1 and I_2 are the ionization energies.

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This relation is available for the different molecules with α and I different, and for identically molecules it becomes:

$$Ed = -\frac{3\alpha^2 I}{4r^6}$$

Because of the fact that the energy variates with r^{-6}, the forces will vary with r^{-7} as in the relation:

$$Fd = -\frac{3\alpha^2 I}{4r^7}$$

fact that shows that they are shorter forces than the ion-ion type of forces.

The depressive forces are attractive forces and the interaction manifests only at the neighboring molecules.

The action of the depressive forces is maintained also at 0^0 K, because the vibrations of the nuclei and of the electronic shells, are maintained at the same temperature.

2. Orientation Forces appear between the polar molecules being attractive forces of dipol-dipol type. In this case the dipoles tend to orientate parallel, this orientation being disturbed by the thermal agitation such that a static distribution is realized.

In the case of two different dipoles, the potential energy varies direct proportional with the square value of the dipole moments of the two substances and inverse proportional with the sixth power of the distances between the molecules:

$$E_0 = -\frac{2\mu_1^2\mu_2^2}{3KTr^6}$$

were μ_1 and μ_2 are the dipoles moments of both molecules; K is the Boltzman's constant, $K = \frac{R}{T}$; T the temperature in Kelvin degrees, r the distances between the molecules and the orientation forces varies inverse proportional with the seventh power of the radius:

$$F_0 = -\frac{2\mu_1^2\mu_2^2}{3KTr^7}$$

In the case of two identical dipoles, the potential energy relation E_0 and the force F_0 becomes:

$$E_0 = -\frac{2\mu^4}{3KTr^6} \text{ and } F_0 = -\frac{2\mu^4}{2KTr^7}$$

3. Induction forces acts between the polar and no polar molecules, sometimes superposing on the orientation ones. The no polar molecules can obtain an extra-induced momentum, under the action of the electric field of the polar molecules, attracted moments of the same sign.

In the case of a single polar substance, the electric field of the dipoles determine an increasing of the separation of the neighbor identically dipoles charges. The Van deer Waals induction forces are

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independent of temperature and varies direct proportional with the polarizability and with the square value of the dipolar momentum and inverse proportional with the seventh power of the distance

$$E_i = -\frac{2\alpha\mu^2}{r^6} \quad \text{and} \quad F_i = -\frac{2\alpha\mu^2}{r^7}$$

Between the polar molecules act in the same time as the three types of Van deer Waals forces and so, the energy and the attraction forces between the molecules will be:

$$E_{v\omega}=E_0+E_i+E_d \quad F_{v\omega}=-\left(\frac{2\mu^4}{3RT}+2\alpha\mu^4+\frac{3\alpha^2 I}{4}\right)\frac{1}{r^7}=-\frac{A}{r^7}$$

Between the non-polar molecules, act only the dispersion forces and as a consequence, the non-polar substances will have the lowest boiling points and melting points, in comparison with the polar substances with a comparable mass.

The weight of the three types of forces, depend on two distinct properties of the molecules: polarizability (α) and the polarity (μ). Thus, between small molecules and strongly polar will act mostly the orientation forces, and between the big ones or non-polar, were the polarizability prevails, will act the dispersion forces (see the table):

Table 1. Contribution of different van der Waals interaction types that appear between some polar molecules

Molecule	Contributions of different types of interactions (%)			E_{vw} (kJ·mol^{-1})
	London	Keesom	Debye	
H_2O	19,00	76,9	4,1	47,31
NH_3	30,00	44,6	5,4	29,60
HCl	81,40	14,4	4,2	17,58
HI	99,50	0,1	0,4	21,14
CO_2	100,00	0,0	0,0	8,75

Through the existence of the Van deer Waals forces are explained the boiling points and the melting points from the upwards to downwards, in the groups of the periodic table, having non-metals (groups VIII, VII, VI)

4. The repulsive forces. Because of the attractive Van deer Waals forces the molecules tend to get very close to each other that determines repulsions between the electronic shells of the molecules, repulsions that determine the appearance of repulsive forces that equilibrates the attractive forces. The repulsive forces varies quickly with the distance so, they disappear completely at big distances, while at the small distances they become permanents, varying inverse proportional with the r^n where n=9-12. In this situation in the Van deer Waals energy expression it must be introduced the repulsive term:

$$E_{v\omega} = -\frac{A}{r^6}+\frac{B}{r^n}$$

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The constant B depends on the nature of the substances and it has a value smaller than A. In the figure below are plotted the repulsive force through the superior curve and through the inferior curve is plotted their resultant. The resultant presents a minimum at an equilibrium distance $r_{v\omega}$ when the attractive forces, equals the repulsive ones, $r_{v\omega}$ being a measure of the sum of the Van deer Waals radii of the two molecules.

The repulsive force manifests in the case of gasses compression, and in the solid state of the molecular substances they balance the attractive forces such that the molecules displaces at a certain intermolecular equilibrium distance. Half of this distance from the molecular crystalline lattices is called van deer Walls radius.

The van deer Waals forces imparts to the molecular substance characteristic properties, because of their strength. Thus, the molecular substances with a big molecular mass and big polarizabilty are or liquids or solids with small symmetry lattices, while the molecular substances with smaller molecular mass are gasses.

The Hydrogen Bond

Another type of intermolecular bonds is the hydrogen bond or the proton bond. It is realized between the protons of the molecule and an strong electronegative atom (F, O, N, Cl) from a neighboring molecule, resulting a molecular associations that can exist specially in liquid state and state, rarely in gaseous state.

This association through hydrogen bonds determines an increasing of the molecular mass, thus, t influences some of the properties like melting points and boiling points and solubility.

The molecular association of the water in lquid gives the best examples of hydrogen bonds or as ice state $(H_2O)_n$ and of the fluorhidric acid an all the state $(HF)_n$. Actually, in the ice, every atom of O of one molecule of water, is covalently bonded of two hydrogen atoms of the molecules, by hydrogen bonds.

Also, in pure diluted solutions or concentrated ones, as well as in crystalline state, or n its hydrates, the phosphoric acid (H_3PO_4) is constituted by tetrahedral PO_4 groups, united between them by hydrogen bonds:

In the $NaHCO_3$ with a catena structure, the trogon groups of CO_3 are united between them by hydrogen bonds.

Another example is the boric acid H_3BO_3 were every oxygen atom from a BO_3 group is bonded by tw- hydrogen bonds.

From here, we can see that the hydrogen bonds have a very important role n the formation of layered crystalline lattices. For example, in the $[Al(OH)_3]_n$ every oxygen atom of one layer, lays on an identically atom from the neighboring layer through hydroxyl groups united by hydrogen bonds.

Also in the $CaSO_4$ $2H_2O$, the bonds between the layers are assured only by the hydrogen bonds from the water molecules

The hydrogen bond was evidenced by the Raman spectra, by nuclear magnetic resonance and neutrons diffraction and X-ray, that showed that the hydrogen atom has a symmetric position with the atom that it bonds, fact that involves that both of the bonds are not equivalent. So, the hydrogen atom is covalently bonded on one of the two atoms, and the other through a special bond of electrostatic nature

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called hydrogen bonds. The table bellow shows some comparative values of the dissociation values in the case of the fluorine and chlorhidric acid.

The hydrogen bond is evidenced by the vibration spectra of the substance too, the free OH group from a molecule having an absorption band characteristic to the electronegative vibration situated in infrared into a domain varying between 3640-3750 cm^{-1}, in function of the nature of the substance that contains this group.

In the [HFH] ion, the hydrogen ion has a symmetrically position from the two fluorine atoms, being at an equal distance from the two atoms. The bonding energy is 113 KJ mol^{-1} and the distance between the two fluorine atoms is of 0.22 nm being smaller that the distance between the two fluorine atoms in the acid, that is of 0.25 nm.

At the beginning it was considered the hydrogen bond as being of electrostatic type because all the substances in which X atom appears strongly electronegative of the molecule, attracts strongly the bond clouds such that the X-H bond is strongly polar with the positive pole localized on the hydrogen atom

The strongly electronegative atom of one neighboring molecule having a pear of non-participating electrons on a hybrid orbital will have a dipolar atomic momentum that will interact with that one of the bonding appearing the orientation forces that tend to realize a collinear arrangement of the two dipolar moments.

This fact I valuable for the hydrogen bonds realized between different molecules X-H,...X-H...

The hydrogen bonds are grouped in strong hydrogen bonds or in protons bonds and weak bonds or hydrogen bridges. In the strong hydrogen bonds, the proton is found at the same distance from the atoms that it bonds, the distance being smaller than 0.25 nm. In this case the energy bond is of 40-80 KJ mol^{-1}.

The hydrogen bonds , have the proton asymmetrically than the atoms it bonds, assuring a distance between them higher than 0.25 nm and an energy bond of 17-30 KJ $mol^{-1.}$

The analysis realizes in many compounds that have hydrogen bonds, confirms the presumption that the bonds are realized with hybrid orbitals. So, in HFH solid the atoms from plane chains in zigzag with angles of 120^0; fact that means that the orbitals of the fluorine are hybridized sp^2.

In the solid water the electron pears non-participating forms bonds of hydrogen being evidenced by the hybridization at the oxygen atom.

The valence bond method explains that the hydrogen bond by the electrostatic attraction that the proton has, that is descreened, on the cloud of the non-participating electron pears from the strong electronegative atom. This way to interpret the hydrogen bond explains the weak bond while the strong bond is interpreted by the existence of some limit structures like:

$F^-...H\text{-}F^-$ F-H.....F^-

The molecular orbitals method gives the same explication to both types of hydrogen bonds and that is : the strong bond is realized by the combination of three atomic molecular orbitals , one of bonding one of antibonding, and one of non-bonding. The electrons will move into the molecular orbitals and non-bonding, this way, being realized the σ bonds that explain the smaller internuclear distances and the big energy bond.

In the delocalized weak bonds it is partial, the electrons are placed partially in atomic orbitals of anti-bonding fact that leads to a partial delocalization on three centers. The occupying of the anti-bonding molecular orbitals with electrons, leads to the canceling of the bonding effect, but, because of the fact that the interaction takes place between the centers, the molecular orbital of non-bonding is trycentic so, the delocalization takes place on all the three centers.

In combinations with the nonsymmetrical bonds in normal state, the proton bond is only partially tricentric, becoming totally trycentric only in excited states, richer in energy that they can reach only few molecules being realized in try dimensional states.

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In the case of intermolecular hydrogen bonds, a linear configuration is not realized, but is realized the most stabile hydrogen bond when the 6 atoms cycles are closed. The hydrogen bridges realized stops the associations of the different molecules and explain the higher volatility of o-derivates and the lower solubility in water.

The formation criteria of the hydrogen bonds of a molecule and an atom strongly electronegative of neighboring molecule, fact that assures the partially ionic character of the bond.

- the atom strongly electronegative, has to have a non-participating doublet into a hybrid orbital
- the X-H bonds and the doublet axis has to be in the same direction, such as the attraction to be maximum.

The presence of the hydrogen bond determines special properties for the compounds. So, it is known that the MP and BP of the molecular substances decrease with the increasing of the molecular mass and the van deer Waals forces in the absence of hydrogen bonds. Comparing this constants at the hydrures of the sixth group of elements, it is observed that the water is an exception. The experimental values are big because there is needed a strong quantity of energy to brake the hydrogen bonds, to which is added the heat quantity, the vaporization or melting.

The a normally MP are fond in other hydrures too, capable to form hydrogen bonds:

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VII. MOLECULAR SPECTRA

VII.1. Introduction

The substances absorb and emit electromagnetic radiations in different ways, depending on the constituting particles nature.

Isolated monatomic elements and ions give lines spectra, the absorption and the emitting of the light is determined by electrons transition, between different levels of atom energy.

In the case of molecules, radicals and poliatomic ions in which atoms are united by covalence, the electronic excitation is not the only one responsible of the light – substance interaction. Characteristic motions of the poliatomic systems appear, that is why the molecules, when absorb or emit energy, they cover a big number of proper energetic states, of rotation or vibration, which excitation energy is very feeble, the spectral lines mix up and give a band spectra.

For example, excited helium gives spectra of lines while the hydrogen molecule, which has two protons and two electrons, give by excitation a band spectra.

In the increasing order of excitation energies, a molecule energy is composed by the translation energy E_t , the rotation energy E_r , vibration energy E_v, and the electronic transitions energy E_e.

$$E = E_t + E_r + E_v + E_e$$

The energy variation of a molecule at excitation is resulted from:

$$\Delta E = \Delta E_t + \Delta E_r + \Delta E_v + \Delta E_e$$

The translation energy variation can be considered as being non quantified and is produced at very low values of the rotation and vibration energies, that is why, is neglected. The rotation and vibration energies variations takes place in a discontinuous way, being characterized each of them by rotation quantum number (v).

To each transition corresponds a spectral domain (Table VII.1). For the rotation spectra the excitation corresponds to microwaves domain, which is the poorest in energy, the rotation levels being excited even at a normal temperature.

The vibration excitation needs energy of 10^3 times higher, the vibration spectra being situated in the infrared spectra. The electronic transition excitation between molecular orbital needs the highest energies, the corresponding spectra being situated in the ultraviolet domain vacuum ($\sigma \rightarrow \sigma^*$) near ultraviolet ($n \rightarrow \sigma^*$ $n \rightarrow \pi^*$) and visible ($\pi \rightarrow \pi^*$). The last ones give the color of the substances containing multiple bonds.

Because, on energy scale, the rotation is in the lowest level, the rotation spectrum accompanies the electronic spectra and the vibration spectra, or they can appear pure. The rotation spectra are the simplest ones, because only lines form them. The vibration spectra have a fine vibration structure, and the electronic spectrum, which is the most complex, has a fine rotation and vibration structure, corresponding to each electronic level. That is why these spectra have a continuous band aspect, which lies, in a certain frequency interval.

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Table VII.1. The principal characteristics of bands spectrum

Spectrum Characteristics	Spectrum		
	Rotation	Vibration	Electronic
Wavelength Domain	10^4μm-1 cm	1μm-25μm	1) 400-800 nm 2) 180-400 nm 3) 100-180 nm
Spectral Domain	Microwaves	Infrared	1) Visible 2) Near UV 3) Vacuum UV
Excitation Energies Kcal.mol^{-1}	$10^{-3} - 10^{-2}$	1 – 10	1) 70 – 36 2) 136 – 71 3) 280 – 161
Characteristic Quantum Numbers	J	ν	
Values of Quantum Numbers	0, 1, 2....	0, 1, 2...	
Selection Rules	ΔJ=±1 (0)	Δν=±1	g→u; u→g 1) σ →σ* 2) n→σ* n→π* 3) π →π*

At the substances being in condense state, liquid and solid, in concordance with uncertainly Heisemberg's relations, an expansion of spectra lines is produced. This contributes to they're amalgamation in bends.

The atoms case, in which the excitation and the return to the fundamental state are completely reversible processes, is very different of that of the molecules, in which because of the chemical bonds fragility, the energetic excitation can produce the dissociation of some bonds or of a hole molecule. That is why absorption molecular spectra are obtained.

Between molecular spectra and the substances structures there is a very strong relation. The study of molecular spectra gives the possibility of some structural characteristics of molecules determinations, which are equilibrium internuclear distances, or covalence length, the dissociation energy of bonds or bonding energies the valences angles etc.

By using standard concentrations, with the molecular spectra in absorption of components concentrations in a sample can be determined.

The absorption molecular spectroscopy has many advantages: the precision in determinations, rapidity, small quantities of substances can be used, the possibility of evidence of some molecular species with very short lifetime etc.

VII.2. Rotation Spectra

By excitation of same molecules with frequencies in microwaves domain, pure rotation spectra are obtained.

The molecules having an electric dipole momentum (polar ones) can give microwaves spectra.

The diatomic homonuclear molecules and polyatomic antrosymetric molecules, non-polar ones (H_2, O_2, N_2, F_2, Cl_2, Br_2, I_2, S_8, P_4, CH_4, CCl_4, SiF_4, SF_6, PCl_5, $Fe(CO)_5$ etc.) don't give microwaves spectra.

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The radiation energy of a molecule can have only definite values, which satisfy the quantification relations, obtained on the base of Schrodinger equation, for the rotation energy. For diatomic molecules, the rotation is:

$$\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}+\frac{2\mu}{\hbar^2}E_r\Psi=0$$

where μ is the reduced mass.

For the relation deduction, the polar molecules will be assimilated with rigid rotator, though considering that the inertia moment (I) of the molecule will not suffer any modifications by exciting the superior rotating state.

For the dynamic rotator, this relation gives the rotating energy around molecular axis:

$$E_R=\frac{\hbar^2}{2I}J(J+1)$$

Because the inertia moment of the molecule around rotation axis is very small ($I = 10^{-36}$ up to 10^{-35} kg/m^3), the excitation energies at rotation level (ΔE_r) are very small to (see Table VII.1).

From the rotation above, we determine the rotation frequency:

$$\tilde{\nu}_r=\lambda_r^{-1}=\frac{\Delta E_r}{hc}=\frac{E_{r2}}{hc}-\frac{E_{r1}}{hc}=\left(\frac{h}{8\pi^2Ic}\right)\left[J_2(J_2+1)-J_1(J_1+1)\right],$$

where: $B=\frac{h}{8\pi^2Ic}$, B being the rotation constant, and we obtain for rotation frequency:

$$\tilde{\nu}_r=\lambda_r^{-1}=B\cdot\left[J_2(J_2+1)-J_1(J_1+1)\right]$$

By applying the selection rule fore the rotation quantum number:

$$\Delta J=J_2-J_1=\pm1$$

and by noting: $J_1 = J$ and $J_2 = J + 1$ we obtain:

$$\tilde{\nu}_r=\lambda_r^{-1}=2\cdot B\cdot(J+1)$$

It was demonstrated that the rotative spectra lines are equidistant.

In reality, for the superior rotation states, by increasing the centrifugal force, the inertia moment increases and the value of **B** decreases, which determines the spectra line to approach.

The last equation should have a corrective term added:

$$\tilde{\nu}_r=\lambda_r^{-1}=2\cdot B\cdot(J+1)-B'\cdot(J+1)$$

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where **B'** is a characteristic parameter for every molecule and it represents the molecule deviation from the rigid rotator model.

For a diatomic molecule formed by mass atoms m_1 and m_2, being at an internuclear distance **r**, the rotation is made around the axis, which passes through the weight center of the molecule, situated at $\mathbf{r_1}$ and $\mathbf{r_2}$ distances of the two nuclei.

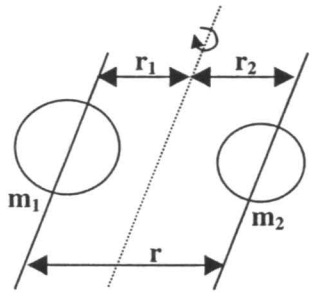

Figure VII.1. Diatomic rigid rotator

For the rigid rotator, the general relation gives the inertia moment:

$$I = \sum_i m_i r_i^2$$

which, applied to a diatomic molecule, give:

$$I = m_1 r_1^2 + m_1 r_2^2$$

But $r_1 + r_2 = r$ and $m_1 r_1 = m_2 r_2$ results that

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$$

Measuring with precision the first line frequency from the microwave spectra, the rotation constant can be obtained.

The covalence length can be obtained from the fine rotation structure of vibration spectra.

VII.3. Vibration – Rotation Spectra

Atoms from molecules, radicals and complex ions, such as particles, which compound the crystalline structures, don't have a fixed pattern in occupying their positions, they move periodically around common equilibrium points. Equilibrium point represents the location between two nuclei for which the energy of the system is minimal.

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VII.4. Vibration – Rotation Spectra For Diatomic Molecules

In diatomic molecules only one type of vibration is possible, the one through which nuclei closer or farther one from another periodically, oscillating around an equilibrium point. This oscillation is called extending vibration or valence vibration, because the bound elongates and condenses successively during a complete oscillation.

VII.4.1. Non Quantified Linear Harmonic Oscillator Model

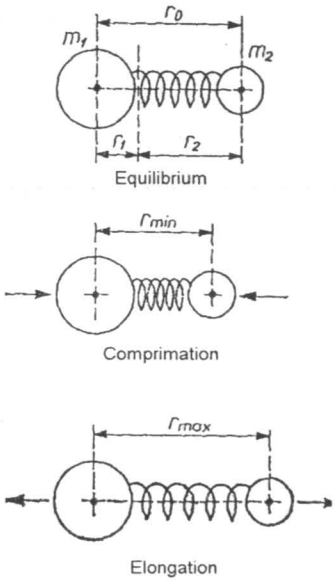

Figure VIII.2.
Linear diatomic oscillator

The diatomic molecule can be assimilated with a linear oscillator, in which the two atoms of mass m_1 and m_2 are united by a chemical bond, which acts like an arch without mass that elongates and condenses periodically. Any displacement of the two atoms from the equilibrium position (r_0) increases the potential energy of the system, in the same way as in mechanical harmonic mass oscillator μ and determines an elastic force appearance F:

$$F = k \cdot (r - r_0) = -kx$$

where **k** is force constant.

In concordance with this, the potential energy can be written:

$$E_v(x) = \frac{kx^2}{2} = 2\pi^2 m \nu_v^2 x^2$$

which is a parabola equation (Figure VIII.3 a) and the frequency of the non quantified linear diatomic oscillator is:

$$\nu_v = (1 - 2\pi)\left(\frac{k}{\mu}\right)^{\frac{1}{2}}$$

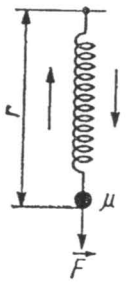

Figure VII.3
Harmonic mass oscillator

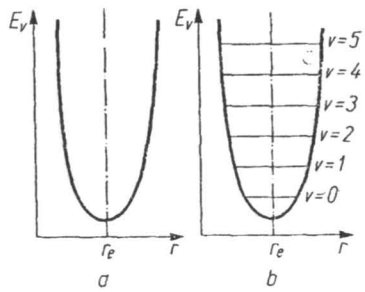

Figure VII.4
Harmonic mass oscillator
a – Non quantified b - quantified

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We can see that, a diatomic molecule can vibrate with a single frequency, determined by the force constant **k** and the reduced mass **μ** of two atoms. In reality, this model is not justified because at the vibration excitation the diatomic molecules have a different behavior.

Table VII.2.
Values for force constant **k** (Nm^{-1})

Length	k
H – H	573
HO – H	842
F – H	966
Cl – H	512
Br – H	412
I – H	314
$H_3C - CH_3$	450
$H_2C = CH_2$	1 090
$HC \equiv CH$	1 720
$H_3C - OH$	530
$H_2C = O$	1 210
$C \equiv O$	1 900

The non quantified linear oscillator model is valuable because its possibility to determine the force constant **k**, being one of the principal purposes of the fundamental spectroscopic research, because the value of **k** increases parallel with the inter-atomic strength and the molecules stability (Table VII.2)

For example, the force constant's value decreases as in sequence: H – F > H – Cl > H – Br > H – I, indicating a decreasing in bonds strength between hydrogen and halogen, as long as electro-negativity difference between the two elements decreases. The value of **k** increases in sequence: C – C < C = C < C ≡ C and in sequence: C – O < C = O < C ≡ O, indicating an increasing of bonding energy of C – C and C – O, parallel with multiplicity bonding increasing.

By determining the fundamental vibration frequency ν_0, we can calculate the force constant and from its value we could obtain precious information regarding the strength and, correspondingly, the nature of chemical bonds. For example, in this mode it have been established the triple bound in carbon oxide, fact confirmed by others experimental data, too.

VII.4.2. Quantified Linear Harmonic Oscillator Model

The elastic force and the oscillation frequency can take any values. The atoms vibrations in molecules are quantified, being determined by the vibration quantum number **v**. This kind of vibration is described by Schrödinger equation for vibration energy:

$$\frac{\partial^2 \Psi}{\partial x^2} \frac{2\mu}{\hbar^2} \left(E_v - \frac{kx^2}{2} \right) \Psi = 0$$

This equation has solution only for some proper value of vibration energy obtained from equation:

$$E_v = \hbar \cdot \left(\frac{k}{\mu} \right)^{\frac{1}{2}} \left(v + \frac{1}{2} \right) = h\nu_v \left(v + \frac{1}{2} \right)$$

where v = 0, 1, 2, 3, …

We observe that the linear quantified harmonic oscillator can exist only for some energetically states.

The vibration is different from zero at v = o:

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$$E_v = h\frac{\nu_v}{2}$$

this is the energy in zero point.

Knowing the selection rules demonstrated by quantum mechanics for v: $\Delta v = \pm 1$ the excitation energy between Ev_1 and Ev_2 levels can be written:

$$E_v = E_{v2} - E_{v1} = h\nu_v\left[\left(v+1+\frac{1}{2}\right)-\left(v+\frac{1}{2}\right)\right] = h\nu_v$$

and for the wave number of absorbed radiation is:

$$\tilde{\nu}_v = \left(\frac{E_v}{hc}\right)\left[\left(v+1+\frac{1}{2}\right)-\left(v+\frac{1}{2}\right)\right] = \frac{E_v}{hc}$$

From this relations result that the vibration spectra contains only one frequency, in IR, not depending on **v**. In fact, the vibration spectra has other transition than vibration corresponding transaction $\mathbf{v} = 0 \rightarrow \mathbf{v} = 1$, which is the most intense, that it indicates the fact that the molecules do not behave like harmonic oscillators.

VII.4.3. Quantified Linear Non-Harmonic Oscillator Model

The vibration spectra, in IR, of diatomic molecules contains a number of bands, from which one is very intense, called frequency of fundamental band, followed by a number of supplementary bands less intense, called harmonica, with a frequency equal to 2, 3, 4, ... times larger than the fundamental frequency ν_0 and they correspond to same transitions for which $\Delta v = 2, 3, 4$ .... These, in fact, are forbidden by selection rules applied to Δv (see Figure VII.5). The deviations from the selective rules are possible because of this vibration and rotation (see Figure VII.6)

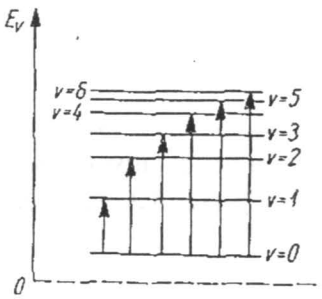

Figure VII.5 Vibration transitions forbidden by selection rules

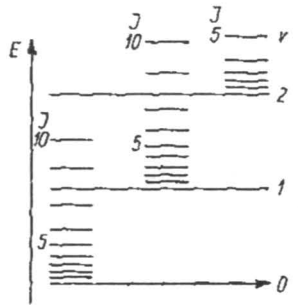

Figure VII.6 Vibration transitions accompanied with rotation transition

Another deviation from quantified linear harmonic oscillator model refers to vibration energy. According to basic equation of quantified linear harmonic oscillator, the potential energy of vibrating system goes to infinity when $\mathbf{v} \rightarrow \infty$. In fact, at diatomic oscillator, there is a limit vibration amplitude corresponding to a maximum intermediary distance, the bond dissociate and the

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potential energy becomes constant. The corresponding energy, **D**, is the dissociation energy of the bond. It is equal in absolute value but different in sign as bond energy.

In the same time, with the increasing of **v**, at high vibration amplitude, the superior energy levels get closer, going to a limit, where the lines are mixing into a single band.

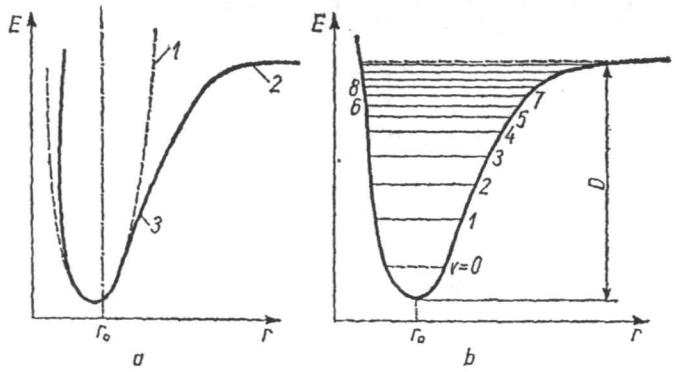

Figure VII.7. The potential energy curve of quantified linear harmonic oscillator
a – comparatively with harmonic non-quantified oscillator curve b – Morse curve for different levels of vibration

With **v** increasing, in the same time, the non-harmonic character accentuates, because the potential energy of the system increases rapidly at bond compression and slowly at bond elongation. That is why the potential energy variation curve has an asymmetric aspect and it is called Morse curve.

For describing quantified non-harmonic oscillator curve (diatomic case) at equation of harmonic model is added a correction factor for non-harmonic character as follows:

$$E_v = h\nu_0\left(v+\frac{1}{2}\right)-\left(\frac{h^2\nu_0^2}{4}\right)\left(v+\frac{1}{2}\right)^2 = h\nu_0\left(v+\frac{1}{2}\right)-y\left(v+\frac{1}{2}\right)^2$$

where **y** is the parameter for non-harmonic character, characteristic to every bond, and **D** is bond dissociation energy.

Vibratory transitions, through absorption of quantum in IR, are possible only for these bonds (or molecules) at which during vibration appear a temporary electric dipole that pulse with fundamental vibration frequency ν_0. In diatomic molecules case this is obtained only for polar molecules. Non-polar diatomic molecules don't give spectrums in IR. At poly-atomics molecules, the polarity condition isn't necessary (see below).

VII.5 Vibration-Rotation Spectrum of Polyatomic Molecules

Polyatomic molecules species have a big number of vibrations possibilities.

The complex vibration movements executed by the molecular species, can be decomposed in a normal vibration bonds series, effected simultaneously.

For molecular specie formed by **n** atoms there are (3n-6) free vibration degrees, if molecules is non-linear and heaving an extra vibration, meaning there is (3n-5) liberty degrees, if the specie is

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linear. The non-linear molecules have (3n-6) vibration ways and the linear one an extra vibration way.

Each vibration is accompanied by a rotation state that forms a "fine structure" of the vibration spectra. That is why the vibration spectra does not appear as distinct lines but as bands shape, which lays in a certain frequency domain.

For non-excited molecules, all vibrations are simultaneously produced at the amplitude corresponding to the zero point of energy ($v = 0$ and $E_v = h\nu_0/2$). For each vibration corresponds a characteristic frequency (ν_0) independent of the other normal vibration frequencies.

When the molecular specie absorbs a quantum in IR, this excites only one normal vibration that one that has its own frequency corresponds to absorbed IR frequency. Its amplitude increases.

The selection rules for the polyatomic species vibration are the same as for the diatomic molecules.

In common conditions, the molecules vibrations, in distinction with rotation, are not excited, the initial vibration state being the fundamental one ($v = 0$). At excitation, fundamental transition is realized ($v = 0 \rightarrow v = 1$).

For the big molecules, especially for one with reduced symmetry, there are a very big number of normal vibrations. This situation is simplified because some bonds, especially that ones that belong to some functional groups (C = O, O – H, NH_2) have characteristic frequencies, which are very less influenced by the presence of other bonds in molecule, their absorption bands could be very easy attributed. These are called "group frequencies". They allow the evidence of some functional groups in molecules, though, the absorption spectra in IR can be used successfully for substances identification and for molecular structure study with new combination, In the table below there are some group frequencies and some characteristic frequencies of same bonds.

Table VII.3. Group frequencies and characteristic frequencies of some bonds.

Bond	Combinations	Absorption bands cm^{-1}
	Group frequencies	
C = O	Aldehydes	1 720 – 1 740
C = O	Ketones	1 705 – 1 725
C = O	Carboxilic Acid	1 647 – 1 721
C = O	Esters	1 725
C – O	Primary Alcohols	1 050
C – O	Secondary Alcohols	1 100
C – O	Tertiary Alcohols	1 150
C – N	Amines	1 030 – 1 300
C = N	Imines and Oxims	1 650
C ≡ N	Nitrils	2 210 – 2 260
	Characteristic frequencies of some bonds	
H – H		4 400
B – H		2 500 – 2 600
C – H		2 800 – 3 300
	CH_4	3 020
N – H		3 200 – 3 400
	NH_3	3 414
O – H		3 200 – 3 700
	H_2O	3 756
F – H	HF	3 950

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VII.5.1 Vibration Types of Polyatomic Molecules

For polyatomic molecules, not as the diatomic molecules, there are more vibration types possible.

For a non-linear tri-atomic molecule, for which 3 x 3 – 6 = 3 normal vibration are possible, two are stretching vibrations or valence vibrations, which are produced in the same way as elongation and compression, and a vibration is produced with the modification of the valence angle and is called deformation vibration.

The two elongation vibrations are not identical. Difference appears because of the vibration phases of the two molecules. A particular case appears when both bonds vibrate in the same phase and a symmetric vibration elongation is produced. When the vibration of the two bonds is not synchronic, that is when on of the bonds is in compression phase and the other elongates, is called asymmetric elongation vibration.

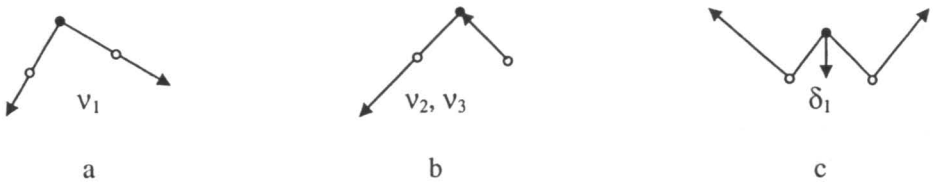

Figure VII.8. Vibration modification of non-linear tri-atomic oscillator
a – symmetrical elongation vibrations b – non- symmetrical elongation vibrations c – deformation vibration

For a linear tri-atomic molecule, for which 3 x 3 – 5 = 4 normal vibration are possible, two of them are elongation vibration and two are deformation vibration. Both deformation vibrations are equivalent.

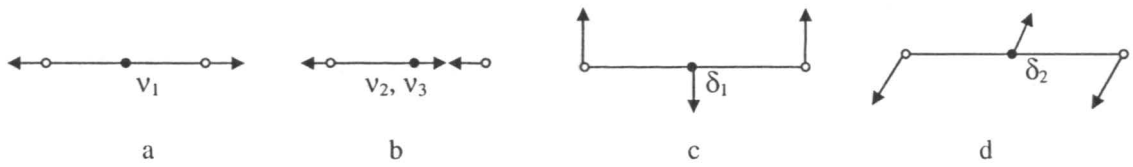

Figure VII.9. Vibration modification of linear oscillator
a – symmetrical elongation vibrations; b – non- symmetrical elongation vibrations; c, d – equivalent deformation vibration

The molecules with a big number of atoms perform complex vibrations that can be decomposed, like in tri-atomic molecules case in normal vibrations, represented by the moving vector indicating the, indicating the direction and sense of atoms movement. For a tetra-atomic molecule, normal vibrations are represented in following figure.

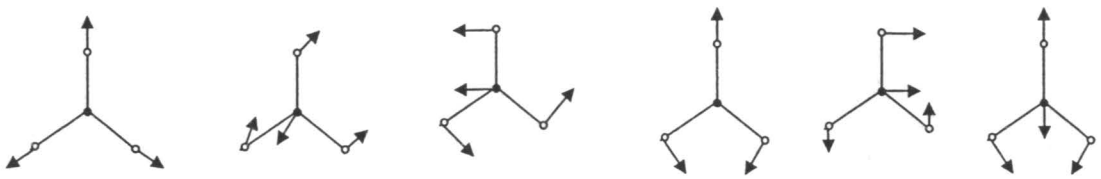

Figure VII.10. Vibration modality of AB_3 type linear tetra-atomic molecular species

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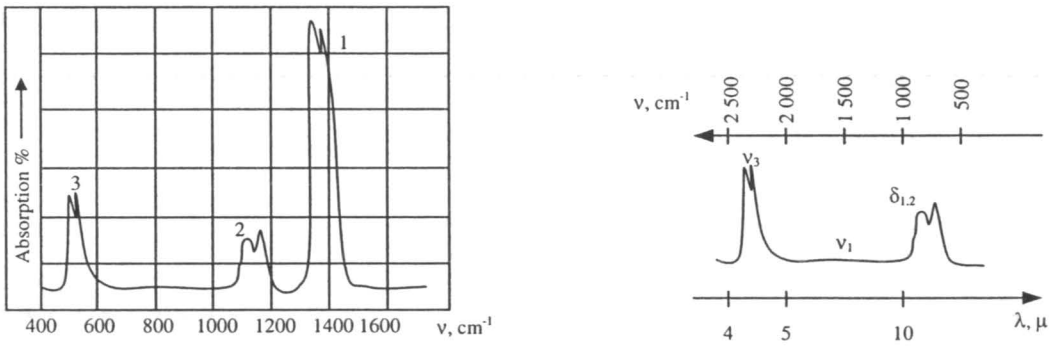
VII.5.2. Infrared Absorption Spectrometry

To study absorption spectrum in IR a special apparatus is used, absorption "spectrophotometers" in IR. Usually, the work is made with a sample of solid substance, in diluted mixture, which does not have absorption bands in the frequency domain where light absorption is significant.

The modern spectrographs record automatically absorption diagram depending on IR radiation frequency. Characteristic curves are obtained. The frequencies for maximum absorption are established.

They are active in infrared, thou they give absorption bands, only normal vibration that determine the electric dipole variation of the molecule.

For example, in polar molecules case, all three vibrations are active in IR (see figure)



VII.11. Absorption spectra in IR
a – of Sulphur dioxide b – of Carbon dioxide

For the linear tri-atomic molecules, symmetric, non-polar, the symmetric elongation vibration is not active in IR because the molecules remain non-polar during a vibration. Only non-symmetric elongation and deformation vibrations are active when in the molecule is introduced a dipole momentum. Two absorption bands appear in IR spectrum of these molecules.

VII.5.3. Raman Spectra

Raman was a physicist who elaborated a new method to obtain rotation-vibration spectra light.

At the Raman spectrum case combined light diffusion phenomenon is very important and is called Raman Effect. If a substance in gaseous state is radiated with a monochromatic light (usuali from UV domain) the photons clink non-elastic with the molecules of the substance. During the contact the photon with initial energy $\mu\nu_0$ can cede a part of its energy to the molecule (during this ν decreases and λ increases), or could gains energy from the molecule (ν increases and λ decreases) if the molecule was excited first. For the first case, in diffused light spectrum (Raman spectrum) appear so-called Stokes lines (red satellites) and for the second case anti-Stokes lines appear (violet satellites), which are less intense, majority of the molecules being in the fundamental state. The difference between the incident frequency (ν_0) and the Stokes line (or anti-Stoke) diffused represents absorbed frequency, Raman frequency respectively. This corresponds to characteristic vibration-rotation frequency of molecule.

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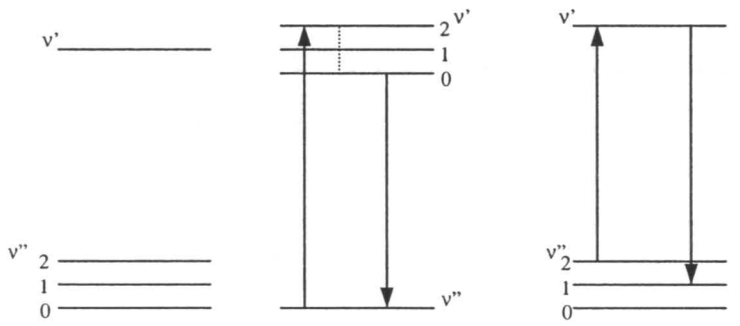
$$\nu = \nu_0 \pm (\nu_v + \nu_r)$$

Apparently, Raman spectra give the same information as IR spectra and microwaves spectra. In fact, for Raman spectra, there are some frequency rules different from the other.

For diatomic molecules, the rule "to o produce a Ramon vibration-rotation spectra is necessarily a variation of molecule polarization" is fulfilled for both polar and non-polar molecules.



a b

VII.12. Possible transition at forming of Raman spectrum lines
a – Stokes b – anti-Stokes

Rotative Raman spectra vibration can be obtained for polar diatoms molecules too, which don't give IR spectra. Also, elongation vibration of central-symmetric molecules gives Raman spectra, inactive in IR.

There are active frequencies in IR spectrum absorption and Raman spectrum, like rotation and vibration frequencies of diatomic polar molecules, vibration frequencies of polar polyatomic molecules etc.

The principal advantage of Raman spectra is the fact that light dispersed frequencies are placed in visible domain, in which the measurement are made with higher precision than microwave and IR spectra.

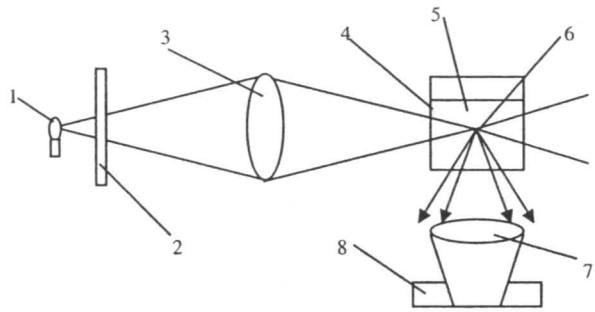


Figure VII.13. Principle scheme of Raman spectrograph
1 – light source (Hg lamp); 2 – monochromator philter; 3 – lens; 4 – vat; 5 – substance in solution; 6 – substance particle; 7 – lens; 8 – spectra-photometer

VII.6. Electronic Molecular Spectra

Through absorption of some radiant energy quantum from ultraviolet invisible domains, the molecules can be electronically excited too. Transitions of bonds electrons are produced from OM, σ and π, of bonding and respectively non-bonding (n).

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Permitted transitions deduced from quantum mechanics are: $\sigma \rightarrow \sigma^*$; $\pi \rightarrow \pi^*$; $n \rightarrow \sigma^*$; $n \rightarrow \pi^*$ (see following figure). We can see that the electrons from OM of bonding or non-bonding pass to OM vacant anti-bonding.

In the case of transition $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$, the excitation reduces the bond and leads to the increasing of the inter-nuclear distance, because OM of anti-bonding are more extended. The force

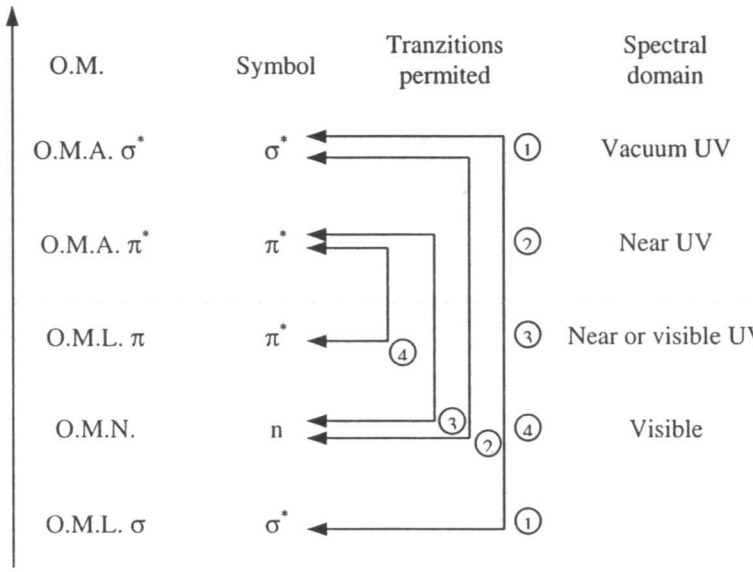


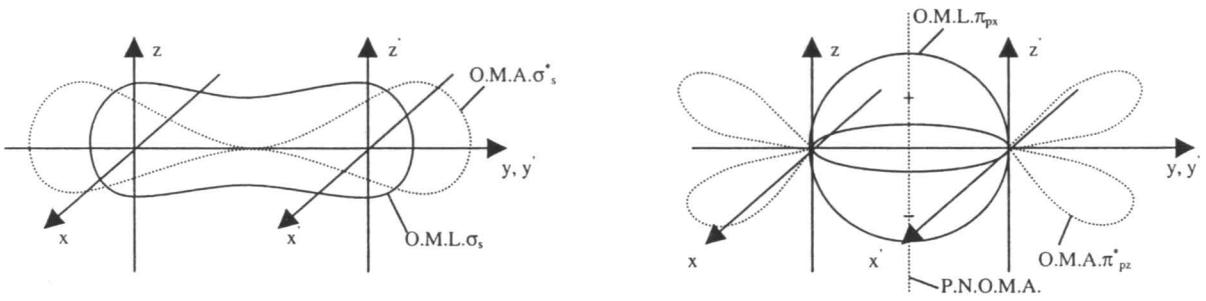
Figure VII.13.
Schematic representation of permitted transaction electronic excitation of molecules

constant **k** and rotation constant **B** decrease. Such transition can be represented through potential energy curves of the two electric levels between which the transition is made; because in the same time the vibration and rotation are excited and give a fine structure of electronic spectrum.

The energy potential curve of the superior level moves in these transition cases to a higher inter-nuclear distance ($r_{02} > r_{01}$) and a superior energy.

If a non-bonding electron is excited, the strength of the bond is small, because the excitation leads to bond dissociation. That is why, from the molecules electronic spectra, bond dissociation energy can be determined. Electronic transmission are possible, because in fundamental state, the molecules, generally, doesn't have electrons on OM of anti-bonding.

Excitation energy are consumed through $\sigma \rightarrow \sigma^*$ transitions, the respective frequencies being in UV and UV vacuum.



VII.14. Molecular orbital representation
a – bond and anti-bond σ; b – bond and anti-bond π

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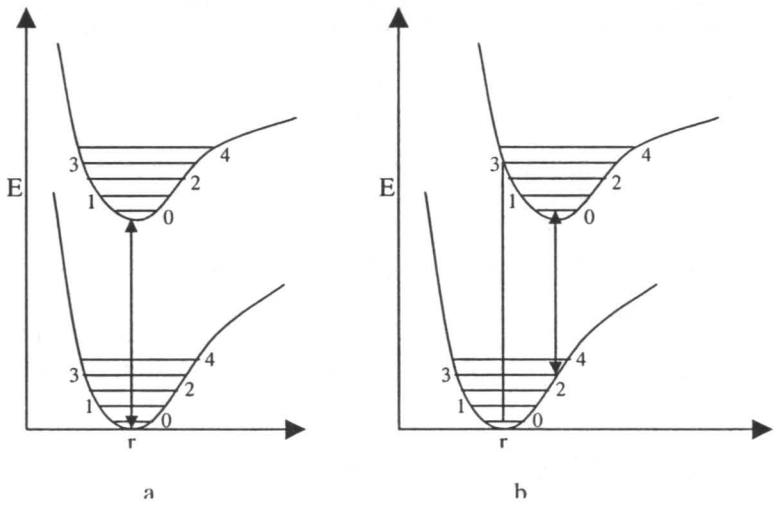
The molecules possessing anti-bonding OM **n** and π is easily excited, their frequencies being in near UV.

The transition $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ are easily excited and give absorption in near UV. That is why the molecules with multiple bonds can be colored.



VII.15. Potential energy curves of two electronic states for a transition $n \rightarrow \pi^*$ or $n \rightarrow \sigma^*$:
a – without modification of inter-nuclear distance: b – with distance modification

VII.6.1. The colors of the substances

Groups of atoms that determine the absorption of the visible light and the color of the substances are called chromatofors. For example, the "nitro" group ($-NO_2$), the "nitroso" group (–NO) and "diazo" group (–N=N–) are such substances. All these groups contain multiple bonds through OM π, with excited electrons by the photons from visible domain of the spectrum, for transitions $\pi \rightarrow \pi^*$.

Absorption bands are influenced by the presence of other bonds or radicals from the molecule. Also, the substances that contain in molecule unpaired electrons and crystals having a big number of delocalized electrons (graphite, metals) for which the excitation energy of the electrons is small, Absorb visible light too.

Poliatomic molecules in which the only possible transitions are $\sigma \rightarrow \sigma^*$ and $n \rightarrow \sigma$ are colorless, the absorption takes place in UV domain of the spectrum. (H_2O,NH_3, CH_4, CCL_4, BF_3, SF_6 etc.)

VII.6.2. Applications of the molecular electronic spectra

The electric spectra of the molecular species cannot be obtained in pure state, the process being complicated by the multiple vibrations that accompany every electronic state.

The electronic excitation always determines the appearance of an electric transitory dipole, which is why, for all the molecules, the electronic spectra, is accompanied by a fine rotation vibration structure. From this spectrum, some molecular parameters can be determined. One of the most important applications refers to the determination of the energy of the covalent bond from the bond dissociation energy.

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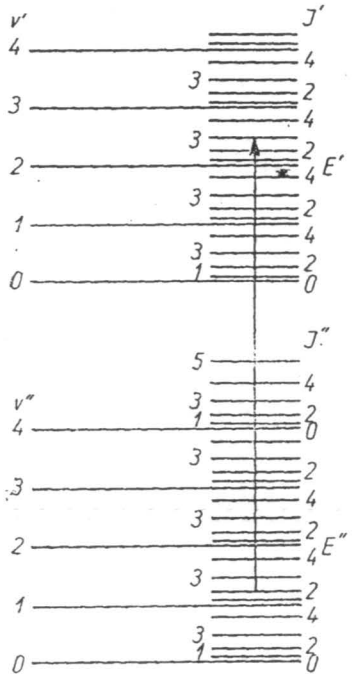

VII.16. Vibration and rotation states for to electronic states E" and E'

Table VII.4. Value of some bond energy

Bond	Energy kJ mol $^{-1}$	Bond	Energy kJ mol $^{-1}$
H – H	430	H – F	563
Li – Li	111	H – Cl	432
Na – Na	75	H – Br	366
K – K	55	H – I	299
C – C	350	Li – H	245
C = C	725	Na – H	202
C ≡ C	886	K – H	182
N – N	159	K – Cl	424
N ≡ N	946	K – Br	378
O – O	143	K – I	319
O = O	402	C – H	415
S – S	266	N – H	391
Se – Se	184	O – H	465
Te – Te	168	C – O	350
Cl – Cl	243	C = O	725
Br – Br	193	C ≡ O	890
I – I	151		

In the table, the values for bonding energy are given and they were determined from electronic spectrum. Also, we can conclude some factors that have a influence upon the strength of the chemical bond:

1) The increasing of atomic radius determines the increasing of the bond energy $H_2 > Li_2 > K_2$; $O_2 > S_2 > Se_2 > Te_2$

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2) The decreasing of electro negativity difference between elements, determines the decreasing of bonding energy. H-F> H-Cl > H-Br > H-I
3) The increasing multiplicity of the covalent bond increases its energy.
C – C < C = C < C ≡ C

VII.7. Magnetic Properties Of The Substances

VII.7.1. The Magnetism Of The Substances

It is known that the substances are made by positive and negative charged particles, which move continuously generating around them an electromagnetic field. The magnetism of the substances is determined by the electronic magnetism and by the nuclear magnetism.

VII.7.2. Electronic Magnetism

The electron behaves in an atom as a magnetic field generator, its orbital motion being characterized by two magnetic vectors. The orbital magnetic momentum vector (μl) and the spin magnetic momentum vector (μs) by combination give the total magnetic momentum vector (μj).

$$\mu_j = \mu_l + \mu_s$$

When the atoms are introduced in a magnetic field, the magnetic momentum vector is orientated in rapport with the exterior field vector (H)

The ratio between the induced magnetic field, or magnetic induction (B), and the inductive magnetic field intensity (H) is called the absolute magnetic permeability (μ)

$$\mu = \frac{B}{H}$$

If μ<1, meaning that B<H, the induced field in the substance is weaker than the inductive field, this phenomenon being called diamagnetism.

If μ>1,meaning that B>H, the induced field in a substance is more intense than the inductor field, this phenomenon being called Para magnetism.

If μ>>1,meaning B>>H, the phenomenon is called ferromagnetism.

The magnetization intensity, or the magnetization of a body I, which is a macroscopic property is direct proportional with the inductive field intensity:

$$\vec{I} = \chi \cdot \vec{H}$$

Where X is the magnetic susceptibility (one-dimensional measure) equal with the induced magnetic momentum:

$$\chi = \frac{\vec{I}}{\vec{H}}$$

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The magnetization intensity and the magnetic susceptibility are macroscopic properties resulted from the sum of the magnetic momentum (μI) in every composing particle of the substance.

Now we can write:

$$\vec{I} = \sum_i \vec{\mu}_i$$

$$\chi = \sum_i \frac{\vec{\mu}_i}{\vec{H}}$$

The sign and the value of the magnetic susceptibility reflect the behavior of the substance in a magnetic field. Though:

- When χ has a negative value, the substance is a diamagnetic one
- When χ has a big positive value, the substance is a paramagnetic one
- When χ has a very big positive value, the substance is a ferromagnetic one.

VII.7.3. Diamagnetism

The diamagnetic substances are that, which, if is introduced in an intense homogenous magnetic field, orientates perpendicularly on the field lines and puts up against their passing, stronger than the vacuum, meaning that the absolute magnetic permeability is sub-unitary: $\mu < \mu_0$ respectively $\frac{\mu}{\mu_0} < 1$.

In a non-homogenous magnetic field the diamagnetic substances are repealed to the minimum density of the field lines.

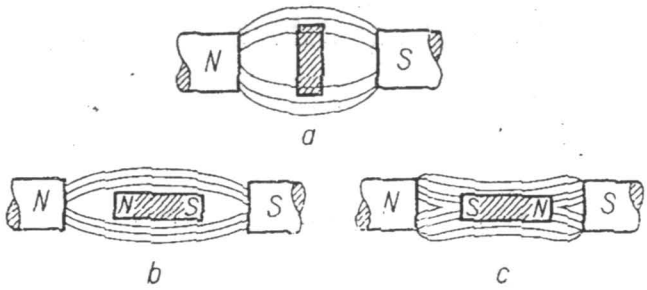

Figure VII.17. Corps in homogeneous magnetic field
a, b – diamagnetic; c - paramagnetic

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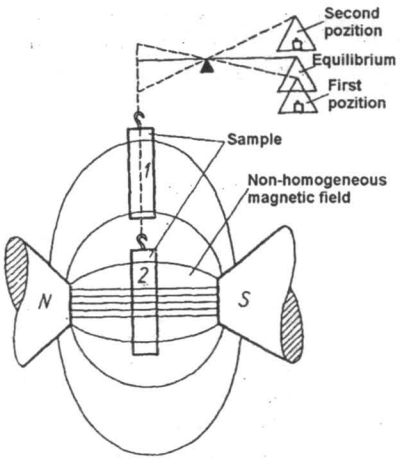

Figure VII.18. Guy balance scheme
Substances behavior in non-homogeneous magnetic field:
first position – diamagnetic substances
second position – paramagnetic substances

Table VII.5. Magnetic molar susceptibility of some substances

Formula	χ_{md}	χ_{mp}	Formula	χ_{md}	χ_{mp}
a. Molecular substances			Br^-	- 36.00	
He	- 1.90		I^-	- 54.00	
Ne	- 7.20		NO^-	- 19.00	
Ar	- 19.40		NO_3^-	- 19.00	
Kr	- 28.00		CO_3^{2-}	- 29.50	
H_2	- 3.94		ClO_3^-	- 30.00	
N_2	- 12.00		BrO_3^-	- 40.00	
O_2		+ 1 700	IO_3^-	- 51.00	
P_4	- 27.00		ClO_4^-	- 32.00	
S_8	- 15.00		SO_4^{2-}	- 40.00	
Cl_2	- 20.00		CN^-	- 13.00	
Br_2	- 30.00		CNO^-	- 20.00	
I_2	- 46.00		CNS^-	- 31.00	
HCl	- 22.00		NaF	- 16.00	
HBr	- 35.00		NaCl	- 30.00	
HI	- 53.50		NaBr	- 43.00	
HNO_3	- 20.00		NaI	- 57.00	
C_2H_6	- 27.00		$FeCl_2$		+ 13 100
C_2H_4	- 12.00		$FeCl_3$		+ 12 100
C_2H_2	- 12.50		$KCr(SO_4)_2 \cdot 12H_2O$		+ 6 300
C_6H_6	- 53.00		$AgNO_3$	- 46.50	
b. Ions and ionic substances			**c. Metals**		
Na^+	- 5.60		Na		+ 12
K^+	- 14.00		K		+ 16
NH_4^+	- 13.00		Mg		+ 6
Ca^{2+}	- 5.50		Ca		+ 44
Cu^{2+}		+ 1 500	Al		+ 6
Cr^{3+}		+ 6 300	Cu	- 6.00	
Cr^{2+}; Mn^{3+}		+ 9 600	Ag	- 22.00	
Fe^{2+}; Co^{3+}		+ 11 900	Au	- 30.00	
Fe^{3+}		+ 14 300	Bi	- 280.00	
Gd^{3+}		+ 26 400	**d. Covalent substances**		
Dy^{3+}		+ 43 000	$C_{diamond}$	- 6.00	
Cl^-	- 25.00		$C_{blacklead}$	- 62.00	

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In these substances a magnetic field is introduced in the opposite sense of the one of the inductor magnetic field.

For one mole from a diamagnetic substance, the magnetization intensity results from the relation:

$$\vec{I} = \chi_{md}\vec{H}$$

Where χ_{md} is the diamagnetic molar susceptibility.

The diamagnetic substances are those which does not have non-coupled electrons. Under the influence of the exterior magnetic field induction currents are produced and they determine the deformation of the populated atomic orbital. With the increasing of the atomic radius the diamagnetism intensifies.

The dependence of the magnetization intensity on the radius of the electronic orbital is given by Langevin's equation:

$$\vec{I} = \chi_{md}\vec{H} = -\left(\frac{Ne^2\vec{H}}{24\pi\varepsilon_0 c^2 m}\right)\sum r^{-2}$$

Were: **N** is Avogadro's number; **e** is the electron charge; ε_0 is the vacuum permitivity; r is the orbital radius; c the speed of light.

Now, we can write:

$$\chi_{md} = \frac{\vec{I}}{\vec{H}} = -\left(\frac{Ne^2}{24\pi\varepsilon_0 c^2 m}\right)\sum r^{-2}$$

By measuring the diamagnetic molar susceptibility we can determine the atomic radii and the electronic structures of the atoms.

Most of the substances contain only orbital with coupled electrons, the tendency for achieving such configuration is main cause of realizing chemical bonds between atoms, especially for atoms belonging to elements from *s* and *p* blocks (representative elements). Also, with atomic hydrogen exception, all substances contain in its structure orbital with coupled electrons. That is way the diamagnetism is in general a property of substances.

VII.7.3. Para-magnetism

The substances are named paramagnetic if, introduced in a homogenous magnetic field they orient parallel with the field lines. In a homogenous magnetic field, the paramagnetic substances are attracted to that part of the field where the intensity is very high. In these substances a magnetic field with high intensity is introduced. The magnetic permeability is $\vec{B} > \vec{H}$ and $\mu > 1$ and the relative permeability is $\mu/\mu_0 > 1$.

The para-magnetism is determined in substances by presence in present particles structure (atoms, molecules, radicals, ions) of unpaired electrons, due to the substance has a own magnetism. This is compound from moments of electronic magnetic vector $\vec{\mu}_s$, $\vec{\mu}_l$ and $\vec{\mu}_j$ in case of a single uncoupled electron and from total magnetic moments $\vec{M}_s$, $\vec{M}_l$ and $\vec{M}_j$ in case of more than one

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uncoupled electron existence. The constituent particles of the para-magnetic substances behave like elementary magnets.

In the absence of the exterior magnetic field, the vectors of the magnetic moments of the constituent particles are chaotically orientated and the substances don't manifest magnetic properties.

When the substance is introduced in a magnetic field the vectors of the magnetic moments of the constituent particles strive to orientate parallel to the field lines, though, a magnetic momentum is introduced. This magnetic moment is proportional to the inductive field intensity (H) and inverse proportional with the temperature (T).

P. Curie elaborated the paramagnetic theory. He showed that the molar paramagnetic susceptibility is inverse proportional to the absolute temperature T:

$$\chi_{mp} = \frac{C}{T}$$

were **C** is Curie constant.

P. Langevin treated the para-magnetism from the quantitatively point of view, by showing (1895) that the magnetization intensity I for one mole of substance is given by the relation:

$$\vec{I} = \vec{H}\left(\frac{N\vec{\mu}^2}{3kT}\right) = \vec{H}\left(\frac{\vec{\mu}^2}{3RT}\right) = \chi_{mp}\vec{H}$$

were μ is the magnetic moment of the constituent particles.

For paramagnetic susceptibility we will have:

$$\chi_{mp} = \frac{N\vec{\mu}^2}{3RT}$$

From these relations we find the physical meaning of Curie constant, which results from expression:

$$C = \frac{\vec{\mu}^2}{3R}$$

meaning that is the square of particles permanent magnetic moment, three times decreased with general gases constant. From this, experimental, we can obtain $\vec{\mu}$ using Curie relation:

$$\vec{\mu} = (3RC)^{\frac{1}{2}} = (3R\chi_{mp})^{\frac{1}{2}}$$

From $\vec{\mu}$ value we can calculate the number of uncoupled electrons using the atoms vector model (normal coupling or Russel – Saunders). The total magnetic moment of a constitutive particle results from relations:

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$$\vec{M}_j = g\left[J(J+1)\right]^{\frac{1}{2}}\mu_0$$

were J is the total intern quantum number ; g is the giromagnetic or Lande factor:

$$g = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$$

This relation was demonstrated in quantum mechanics.

For the cations of "d" and "f" elements that form numerous paramagnetic combinations the contribution of the orbital magnetic momentum is neglected in comparison to the spin contribution. Though we can write: L ≅ 0 and J = S such that:

$$g = 1 + \frac{S(S+1)+S(S+1)}{2S(J+1)} = 2$$

and

$$\mu_S = 2\left[S(S+1)\right]^{\frac{1}{2}}\mu_0$$

If we denote with "n" the number of the umpired electrons in an atom, ion or molecule, each of them have s=1/2 spin, the total spin results S=n/2. We obtain:

$$\mu_S = \left[n(n+2)\right]^{\frac{1}{2}}\mu_0$$

For the cations of the "d" elements the magnetic moment calculated with this relation is in accordance with the values obtained after the experimental measurements are in the following table:

Table VII.6. Magnetic moments of "3d" cations

Electrons number		**Quantum numbers**		**Magnetic moments expressed, $\vec{\mu}_0$**			**"3d" cations**
3d	**odd**	**S**	**L**	$\vec{\mu}(S+L)$	$\vec{\mu}S$	$\vec{\mu}_{ef}$	
3	3	3/2	3	5.20	3.87	3.68 – 4.00	V^{2+}; Cr^{3+}; Mn^{4+}
4	4	2	2	5.48	4.90	4.80 – 5.06	Cr^{2+}; Mn^{3+}
5	5	5/2	0	5.92	5.92	5.20 – 6.00	Mn^{2+}; Fe^{3+}
6	4	2	2	5.48	4.90	5.00 – 5.50	Fe^{2+}; Co^{3+}
7	3	3/2	3	5.20	3.87	4.40 – 5.20	Co^{2+}
8	2	1	3	4.47	2.83	2.80 – 4.00	Ni^{2+}
9	1	½	2	3.00	1.73	1.80 – 2.20	Cu^{2+}
10	0	0	0	0	0	0	Zn^{2+}; Cu^{+}

If we replace μ with μ_s we obtain:

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$$\chi_{mp} = \left(\frac{\mu_0^2}{3RT} \right) n(n+2)$$

With the relation we can calculate the number of unpaired electrons at different temperatures. For the paramagnetic substances the value of χ_{md} is small and it can be neglected.

VII.7.4. Ferromagnetism

It is a property of the atomic systems, actually of some crystalline metallic lattices or of ionic types.

Through ferromagnetism we will understand a powerful magnetization in the magnetic field of some crystalline substances with very high magnetic permeability.

Ferromagnetic substances strive to a magnetic saturation. The magnetic susceptibility varies with H.

The ferromagnetism can be explained through parallel orientation in a perfect order of the magnetic vectors of the atoms or ions in the magnetic field.

Table VII.7. Ferromagnetic, anti-ferromagnetic, ferrimagnetic substances

Substance	Characteristics	Substance	Characteristics
A. Ferromagnetic crystals	Curie temperature (K)	C. Anti-ferromagnetic crystals	Neél temperature (K)
Fe	1 043	Mn	100
Co	1 400	Cr	308
Ni	631	MnO	116
Gd	292	FeO	198
CrO_2	392	CoO	291
MnAs	318	NiO	525
MnSb	587	Cr_2O_3	307
MnBi	630	MnS	160
Cu_2MnAl	710	FeF_2	79
MnB	578	$FeCl_2$	24
UH_3	180	$FeCO_3$	35
B. Ferromagnetic alloy	Composition	D. Ferrimagnetic crystals	Curie temperature (K)
Permalloy	70 – 80 % Ni;	$MnFe_2O_4$	573
	30 – 20 % Ni	Fe Fe_2O_4	858
Alnico 24	24% Co; 14% Ni; 8% Al;	Co Fe_2O_4	793
	3% Cu and Fe	Ni Fe_2O_4	858
Remalloy	12% Co; 17 ... 20 % Mo	Cu Fe_2O_4	728
	and Fe	Mg Fe_2O_4	713

By increasing the temperature of the substance, the thermal agitation intensifies and the ferromagnetism is decreased.

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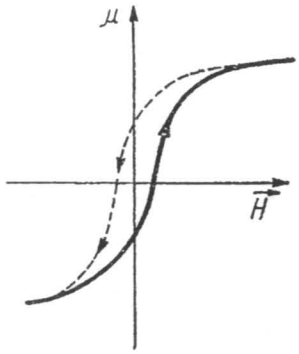

Figure VII.19. Magnetizing and demagnetizing of ferromagnetic substances

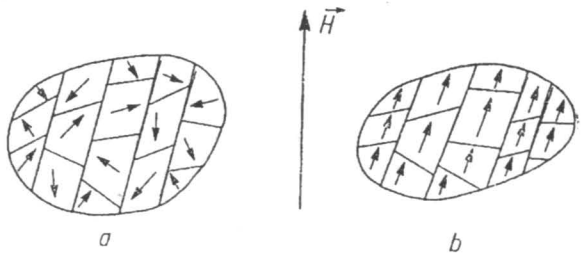

Figure VII.20. Schematic representation of ferromagnetic substances magnetization
a – elementary magnets orientation before magnetization;
b – elementary magnets orientation after magnetization.

At a given temperature, the ferromagnetism disappears and the substance becomes paramagnetic. This temperature is called Curie point. Introduced again in a magnetic field, the substance magnetizes again.

The number of ferromagnetic substances is very small but they have a very big importance in electronics, electro-ethnics and other domains.

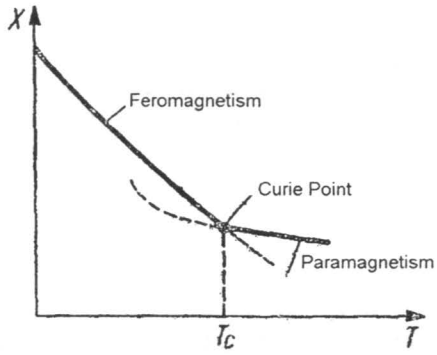

Figure VII.21. Variation function of temperature of ferromagnetic substances magnetism

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VII.7.5. Anti-ferromagnetism

It is a property related to the ferromagnetism. Contrary to ferromagnetic substances, at a normal temperature, the anti-ferromagnetic substances behave like paramagnetic substances into a magnetic field.

With the increasing of the temperature they magnetize in magnetic field and they reach a magnetic saturation called Neél point, after this point the substances are slowly demagnetized. The anti-parallel orientation of the elementary magnetic moments at a normal temperature explains this phenomenon. When the temperature increases the possibility to free rotation of the constitutive particles appear. The magnetic vectors get parallel orientated and the substance magnetizes slowly until reaches Neél's temperature, where, the vectors are again very disordered.

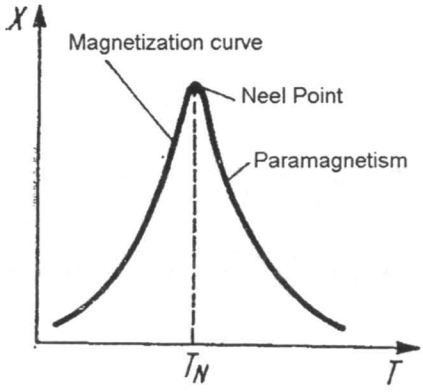

Figure VII.22. Variation function of temperature of anti-ferromagnetic substances magnetism

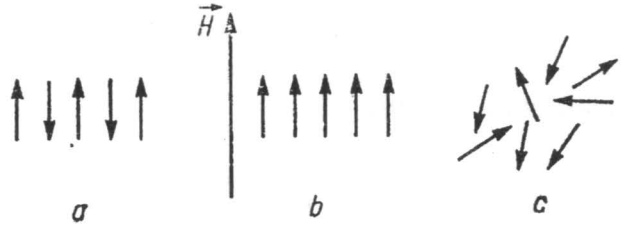

Figure VII.23. Elementary magnets vector orientation at anti-ferromagnetic substances
a – before magnetization; b – after magnetization; c – after Neél point.

Some anti-ferromagnetic substances are: Cr, Mn, Fe, Co, N.

VII.7.5. Ferrimagnetisms

Represents a number of magnetic properties of "ferrites" due to the anti-parallel arrangement of the atoms. The number of different orientated vectors is not equal.

For $FeFe_2O_4$ or Fe_3O_4 the arrangement of the magnetic moments are represented in the figure below:

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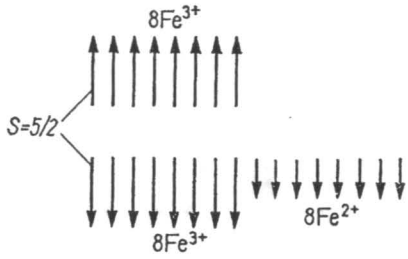

Figure VII.24. Orientation scheme of magnetic vectors in ferimagnetic network of Fe_3O_4

The "ferrites" are used in high frequencies techniques, automatics, telecommunications etc.

VII.8. Electric Property And The Molecular Refraction Of The Substances

VII.8.1. The Behavior Of The Substances In The Electric Field

In function of their behavior in the electric field, the substances can be: electric conductors and insulators or dielectrics. In the first category the substances have free electric charges (electrons), like metals, alloys, and graphite and they are also first order conductors. From the second order conductors we can name the ions, solutions of salts or ionized acids, which, under the action of an electric field, they can move and produce the electric charges transport. If the substances don't have free electric charges, they cannot produce the electric charge transportation and they will behave like insulators or dielectric (like non-ionized molecules gases and solids.)

The presence of a dielectric in an electric field reduces the field's intensity and enlarges the capacity of the condenser in rapport to intensity and the vacuum condenser capacity, with a quota share, characteristic for each of the dielectrics, called dielectric constant.

$$\varepsilon = \frac{E_0}{E_D} = \frac{C_D}{C_0} > 1$$

where E_0 is the field intensity, C_0 – condenser capacity in vacuum, and E_D and C_D – the same in the dielectric's presence, ε – dielectric constant.

VII.8.2. Polarization Phenomenon in Electric Field

The macroscopic phenomenons that appear at the introduction of the dielectric substances into an electric field have tier origin in the polarization phenomenon produced at the level of the micro particles that compose the substance. Thus in electric field the component particles of the dielectrics deform themselves because of the electronic shell is misplaced to the anode and the nuclei to the cathode of the condenser. The induced electric moments are opposite than the inductor electric field and this fact determines the diminution of the condenser capacity.

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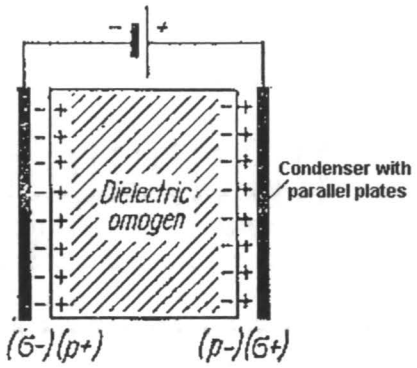

Figure VII.25. Dielectric in electric field

There are two types of polarization: misplacement polarization and orientation polarization. The first one is present at all the micro particles when the substance is in an electrostatic field and the second is present only at polar molecules.

VII.8.3. Misplacement Polarization Clausius And Mosotti's Equation

The misplacement polarization P_D is determined by two kind of field particles interactions. The first one is the electronic polarization P_E and it is present due to the misplacements in different ways of the electronic shell of the atoms and of the atomic nuclei. This polarization is produced at

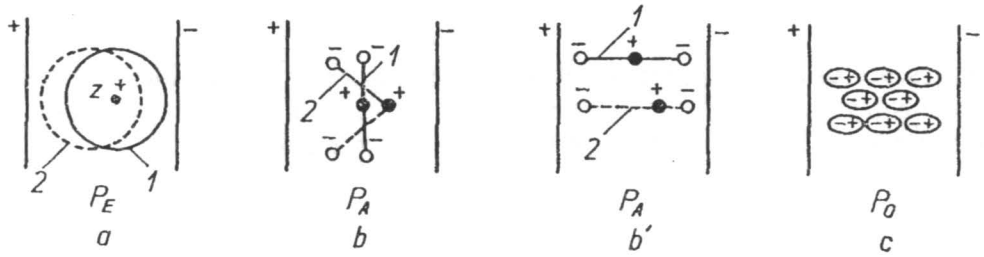

Figure VII.26. Schematic representation of polarity in electric field
a – electronic polarization; b – b' – atomic polarization; a and b – movement polarization; c – orientated polarization; 1 – molecule before polarization; 2 – after polarization.

isolated atoms and at atoms involved in chemical bonds with other atoms too. The second one is the atomic polarization P_A and it is produced at the molecules formed by polar bonding in which the most electronegative atoms are over screened being more attracted to the anode. The atoms with smaller electro negativity are unscreened being more attracted to the cathode. The components of the displacement polarization determines a separation of the positive and negative charges, from the mono- and poyatomic molecules, that is the appearance of an electric dipole momentum at the non-polar molecules, or the increasing of the electric momentum at polar molecules.

The induced electric momentum ($\vec{\mu}_i$) depends directly proportional on the inductive field intensity.

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$$\vec{\mu}_i = \overline{\alpha} E$$

were $\overline{\alpha}$, proportionality factor is equal with the induced electric momentum in a molecule by a field with its intensity equal to unity called molecule polarizability.

The polarizability of the molecules is a measure of the electric deformability of the molecule and it is characteristic to every substance.

Because of the chaotic movement of the molecules the polarizability has a medium value. The medium polarizability of the molecules can be determined from the dielectric properties of the substance between the medium polarizability α and the dielectric constant ε. So, if between the armatures of a condenser with vacuum electrostatic field intensity E_0 an homogenous dielectric is introduced on its surface will appear electric charges with a different sign than that of the condenser poles. This is produced because of the dipolar electric momentum induced in every molecule. Inside of the dielectric, the induced moments set off each other and the charge manifests only on the contact surfaces between the armatures and the dielectric.

On the surface of the dielectric, an orientated electric field is produced, in the inverse sense than that of the exterior field, which decreases the field intensity and increases the capacity of the condenser.

The electric charge appeared on the surface unity of the dielectric is called polarization intensity or ***p*** polarization. An elementary dielectric cube can be assimilated in accordance with the relation for a dipolar momentum $\mu = e \cdot l$, with an electric dipole with an electric dipole moment ***p***.

If the elementary volume of the dielectric has N_0 molecules, p represents the sum of all N_0 induced dipolar moments:

$$p = N_0 \cdot \mu_i = N_0 \overline{\alpha} E .$$

If we consider the dielectric as being a perfect continuous homogenous medium, some relations from the electrostatics may be applied, the field intensity in the condenser having parallel plane plates in vacuum is:

$$E_0 = 4\pi\sigma ,$$

were σ is the charge on the plate unity surface. The field intensity in the dielectric decreased because of the induced charges on the free surfaces results from:

$$E_D = E_0 4\pi \cdot p$$

$$E_0 = E_D + 4\pi \cdot p \cdot N_0 \overline{\alpha} = 4\pi \cdot p \cdot \chi$$

were χ is the dielectric susceptibility.

We observe that:

$$\varepsilon = 1 + 4\pi \cdot N_0 \overline{\alpha} = 1 + 4\pi \cdot \chi$$

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Because in fact, the dielectric is a discontinuous medium the field intensity that acts upon the molecules is bigger than E_D. If we consider the molecules as being spheres, for the effective field intensity E we can write:

$$E = E_D + \left(\frac{4\pi}{3}\right)p$$

By eliminating E_0 we obtain:

$$4\pi \cdot p = E_D(\varepsilon - 1)$$

And by eliminating E_D we obtain:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} \cdot \frac{p}{E}$$

Because we know that N_0 is the elementary volume, equal to: $\frac{N}{V}$ and V can be written in function of d-density and M-molecular mass: $\frac{d}{M}$ we have:

$$P_M = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} \cdot \frac{N\mu_i}{E} = \frac{4\pi}{3} \cdot N\bar{\alpha}$$

known as Clausius and Mosotti's equation.

This equation was deduced taking in consideration only displacement polarity:

$$P_M = P_D = P_E + P_A = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} \cdot N\bar{\alpha}$$

From this relation results a impedance of molar polarity of temperature for non-polar molecules, from which electric dipole momentum $\mu = 0$.

VII.8.4. The Correlation Between The Molecular Structures And The Displacement Polarization

In the electrostatics is demonstrating that the polarizability of a metallic sphere is equal with the radius square. By assimilating the molecules with metallic spheres being $\alpha = r^3$ we find that the molar polarization equals:

$$P_M = \frac{4\pi}{3} \cdot Nr^3$$

Now, we can determine the molecular radius as the critical size of the particles.

By measuring the capacitance of a condenser in vacuum and in the presence of the dielectric, we can calculate the medium molecular polarizability.

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In the table below, we have the polarizability of some molecules and some ions.

Table VII.8. Polarizability of some ions, molecules and bonds

Formula	α	Formula	α	Formula	α
I. Ions		**II. Molecules**			
H^-		He	0.201		
F^-	1.05	Ne	0.390	NH_3	2.23
Cl^-	3.69	Ar	1.62		
Br^-	4.81	Kr	2.46	CH_4	2.63
I^-	7.16	Xe	3.99		
O^{2-}	2.75	H_2	0.80	CCl_4	10.53
S^{2-}	8.60	F_2	1.16	CO_2	3.04
Se2v	11.20	Cl_2	4.60	CS_2	7.34
Li^+	0.029	Br_2	6.90	**III Bonds**	
Na^+	0.179	I_2	11.00	– C	1.03
K^+	0.83			C =	1.34
Rb^+	1.40	O_2	1.70		
Cs^+	2.42	S_8	24.00	– C ≡	1.42
Be^{2+}	0.008				
Mg^{2+}	0.094	N_2	1.75	– N	0.97
Ca^{2+}	0.47	HF	0.98		
Sr^{2+}	0.86	HCl	2.64	N =	0.90
Ba^{2+}	1.55	HBr	3.62	N ≡	0.83
Zn^{2+}	0.50	HI	5.45		
Cd^{2+}	1.15	H_2O	1.49	O –	0.69
Hg^{2+}	2.45	H_2S	3.80	O =	0.85

We can see that the polarizability increases parallel with the dimensions of the particles, like in this example: $F^- < Cl^- < Br^- < I^-$; $Li^+ < Na^+ < K^+ < Rb^+$; $CO_2 < CS_2$. The exterior electronic shell of the atoms can explain this, because it becomes more and more diffuse. Also, the presence of the d exterior orbital increases the possibility of deformation of the electric shell. We explained the increasing of the polarizability for the elements from the third group and for their combinations in comparison with the second group. For example, from N to Ar the polarizability increases over four times.

In periods, with the increasing of the effective nuclear charge (Zeff) the atomic radius decreases; thus, the medium polarizability decreases, for example, the polarizability decreases in:

$$CH_4 > NH_3 > H_2O > HF$$

VII.8.5. The Orientation Polarizability

It was demonstrated that in the case of polar molecules, the molar polarization depends on the temperature. At this molecule, in the electric field, a supplementary polarization appears, called orientation polarization and it is determined by the parallel orientation of the molecule dipoles.

The orientation polarization is big as long as the permanent dipole momentum of the molecule is big and the temperature has a law value.

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Between orientation polarization and para-magnetism there is a perfect analogy. So, Debye extended the Langevin's theory of the para-magnetism for the polarizability orientation.

The value of the medium component of the electric dipole is:

$$\bar{\mu} = \left(\frac{\mu^2}{3kT}\right)E$$

The total momentum in the field directions is:

$$\mu_t = \mu_1 + \bar{\mu} = \bar{\alpha}E + \left(\frac{\mu^2}{3kT}\right)E = E\left(\bar{\alpha} + \frac{\mu^2}{3kT}\right)$$

Now, we can write:

$$P_M = P_D + P_0 = P_A + P_E + P_0 = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} =$$

$$= \left(\frac{4\pi}{3}\right) \cdot N\bar{\alpha} + \left(\frac{4\pi}{3}\right) \cdot N \cdot \left(\frac{\mu^2}{3kT}\right) =$$

$$= \left(\frac{4\pi}{3}\right) \cdot N \cdot \left[\bar{\alpha} + \left(\frac{\mu^2}{3kT}\right)\right]$$

This is Debye's relation for molar polarizability of the polar substances. For the non-polar molecules $\mu = 0$.

VII.8.6. Molar Refraction

In concordance with the electromagnetic theory, there is dependence between the dielectric constant of a substance and the refraction index:

$$\varepsilon = n^2$$

If we replace by $\mathbf{n^2}$ the dielectric constant we obtain for the molar refraction:

$$R_M = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = \left(\frac{4\pi}{3}\right) \cdot N\bar{\alpha}$$

By measuring the visible and infrared refracting index we obtain the value for electric polarization P_E and for the displacement polarization P_D. Now, we can separate the compounds of the polarization like this:

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$$R_M(visible) = P_E,$$
$$R_M(IR) = P_D = P_E + P_A,$$
$$P_A = R_M(IR) - R_M(visible),$$
$$P_M = P_D + P_0 = P_E + P_A + P_0,$$
$$P_0 = P_M - R_M(IR).$$

The molar refractions can be determined with high precision by measuring the refracting index with a very simple method.

VII.8.6. The Correlation Between The Molar Refraction And The Molecular Structure.

A very important property of the molar refraction is its additive character. For a specific substance the molar additive refraction is composed additively from the molar refractions contributions of the constitutive atoms and ions: $R_M = \Sigma R_A$ or $R_M = \Sigma R_I$ were R_A and R_I are the atomic and ionic refractions. The molar refractions calculated are in concordance with the determined ones from the tables below:

Table VII.9. Atomic and bonds refractions

Atom	Refraction	Bond	Refraction
H	1.100	H – H	2.080
F	0.997	O – H	1.880
Cl	5.967	N – H	1.870
Br	8.865	C – H	1.705
I	13.900	C – C	1.209
O (hydroxylic)	1.525	C = C	4.150
O (carbonylic)	2.221	C ≡ C	6.025
N (primary amine)	2.322	C – C	1.420
N (nitrilic)	3.118	C = O	3.420
C –	2.418	C – N	1.550
C =	1.733	C – F	1.600
C ≡	2.398	C – Cl	6.570
		C – Br	9.47
		C – I	14.510

Table VII.10. Molar refractions

Substance	R_M calculus formula	R_M (theoretic)	R_M (calculated)
H_2O	$R_M(H_2O) = 2R_A(H) + R_A(O)$		
	$R_M(H_2O) = 2\,R_M(OH)$	3.76	3.71
CO_2	$R_M(CO_2) = R_A(C) + 2\,R_A(O)$		
	$R_M(CO_2) = 2\,R_M(CO)$	6.84	6.71
$CHCl_3$	$R_M(CHCl_3) = R_A(C) + 3R_A(H) + R_A(Cl)$		
	$R_M(CHCl_3) = R_M(CH) + 3R_M(CCl)$	21.41	21.25

The molar refraction represents the deviation from the additive in the case of the molecules with multiple functionalities. For example, in the case of conjugated double bonds, the molar refraction is bigger than that calculated from the atomic refractions and from the bonds and in the case of aromatic cycles it is under the calculated value due to the high stability of the aromatic

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systems. So, molar refraction study gives precision regarding molecular structure. This was the first physic-chemical method used in molecular structure research. In the last two decades it decreased in importance due to the development of other methods, more accurate for example the spectral method.

Deviation from molar additive refraction presents also the ionic combinations, following the mutual polarization phenomenon between anions and cations.

Thus, we distinguish a series of rules:

- polarizing power of the cation on the electronic shell of anion gets grater if the radius is smaller and has a big charge;
- at equal radius and charge, the ions with inert gas cover have minimum polarizing action, and those with d substratum during completion a bigger one. Polarizing power is maximum at cations with external configuration ($s^2p^6d^{10}$ for example: Zn^{+2}; Cu^+; Cd^{+2} etc.) and s^2 (for example ZnS, AgI, $SnCl_2$, $CdCl_2$ etc);
- as long as polarity action of a cation is bigger the modification of the molar polarity and refraction of ions with opposite charge is bigger.

By using the relation $\varepsilon = n^2$ we could calculate the polarity of chloride ion from mentioned compounds:

- at ions with same charge of elements from the same block polarity increases as follows: $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ and at halogen ions as follows $F^- < Cl^- < Br^- < I^-$;
- at izoelectronic ions polarity is bigger or the positive charge is smaller. For example: $N^{3-} > O^{2-} > F^- > Ne > Na^+ > Mg^+ > Al^{3+} > Si^{4+}$

Table VII.11. Molar refraction of chloride ion function of polarizing action of some cations.

Cation	H^+	Li^+	Na^+	K^+	Cs^+
$\mathbf{R_M(CL^-)}$, **cm**^{3}	6.67	7.40	8.00	8.60	8.97

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CHAPTER VIII
AGGREGATION STATES

GENERALITIES

The properties of the molecules, of the ions or of the atoms are not usually established on individual particles but on systems of macroscopic particles .A system of macroscopic particles can present itself in a solid, liquid or gaseous state.

An aggregation state is conditioned by two factors:

- the interactions between particles (molecules, ions, atoms) which lead to a structural ordered succession of the particles;
- the thermal agitation the particles which opposes to the influence of the ordered succession of the interactions.

By the concept of the 'interactions' we understand: all the attraction and rejection forces that appear between particles (molecules, ions, atoms).

If between particles does not appear any interaction and if the own volume of the particles is negligible in comparison with the total volume, then the macroscopic properties of the system are determined only by the thermal agitation; it is the case of an ideal gas. This limit state is reached at a very low pressure and at a very high temperature, when the density within particles is small and the distance between particles is very long, such that there can not manifest interactions. Most of the times the interaction must be taken into account; it is the case of a real gas.

The second limit states is characterised by strong interactions and zero thermal agitation; it is the case of the ideal solid. In these conditions, the properties of the ideal solid should not be dependent of the temperature. This ideal state is never reached; the cause would be the perturbation of the perfect succession of the particles by their oscillations, which appear at absolute zero temperature. So, there exist a minimum oscillation energy- the energy of point zero. This is why the real solids can only approximate the ideal state.

In the liquid aggregation state, which is between the state of real gas and the state of real solid, the interactions between particles can be so intense as the ones at the solids. So, the particles have a certain orientation but ,in consequence of their mobility, they change the form of the liquid. Both solids and liquids have high densities, constant volumes and low thermal compressibility and dilatation. Both gases and liquids have translation motions of particles.

The transformation of a substance from one aggregation state to another is due to the modification of the speed motion of the particles and of the dimension of the spaces between them.

Thus, through the raising of solid temperature, its particles become more and more agitated and more and more oscillating, but without displacing from their fixed positions. Reaching the melting point the agitation becomes so intense that the particles can't maintain a fixed and regular arrangement. Consequently, the melting point of a substance represents the moment when, because of the exterior heating, the quantity of accumulated heat within a substance is large enough to transform the

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oscillatory motion of the particles in irregular motion. The substance passes from solid state to liquid state.

When the temperature of a liquid increases the agitation of the particles becomes so strong at one point that the forces of mutual attraction, which maintain a certain distance between molecules, grow weak ,part of the particles detaches from the others and, in free state ,they tend to occupy the available space. The substance passes from liquid state to gaseous state.

Similarly, as a result of decreasing of the temperature of a gas, the agitation of the particles is lower , the force of mutual attraction intensifies, the particles of the substance bring nearer until a certain distance ,and the substance passes from gaseous state to liquid state.

At a greater decreasing of the temperature, the agitation of the particles weakens ever more until they occupy fixed positions round about they vibrate: the substance passes from liquid state to solid state.

VIII.1. **GASEOUS STATE**

A mass of gas is characterised by three parameters :pressure, volume and temperature. These physical quantities are called variables(or parameters) of state.

In specific quantities of substance the variables of state are interdependent. For example ,if the volume of a gas increases at a constant temperature the pressure is lower, so it is dependent on the volume .The mathematical relation of the state variables represents the thermic equation of gas state. Thus, if we denote the pressure with p, the volume with V and the absolute temperature with T, then between these physical quantities there exists the functional relation:

$$F(p,V.T)=0$$

from which , for example, the pressure can be expressed as function of volume and temperature:

$$p = f(V,T).$$

In the case of gases, after the interactions between particles ,there is a distinction between ideal gases (or perfect) and nonideal gases.

1.1. Ideal gases .

1.1.1. BOYLE-MARIOTTE's Law.

The low Boyle-Mariotte shows that: at a constant temperature the volume of a determined mass of gas is inversely proportional with the pressure which the gas is under.

For example, if the pressure exerted on 2l of gas doubles , the volume of the gas decreases until reaches 1l. Mathematically, the expression is written:

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$$V_1 / V_2 = p_1 / p_2 \qquad \text{or} \qquad p_1 V_1 = p_2 V_2.$$

where V_1 and p_1 represent the initial volume and pressure of the gas, V_2 and p_2 –the new volume and pressure. So, at a constant temperature the product between the volume and the pressure of a certain mass of gas is constant:

$$pV = k; \qquad k = \text{const.}$$

k is a variable constant for a certain temperature (and a certain quantity of gas). If we make a graphic representation to prove the dependency of the pressure on the volume we obtain for each temperature an equilateral hyperbola. Such curves are named isotherm curves.

The law of Boyle- Mariotte is applicable in the domain of low pressure and normal temperature. At very high pressures all gases exert deviations of this law. Thus, if we take the example of nitrogen, at an 1 atm pressure the product pV=1.000 1atm, at 1000 atm pV=2.0685 1atm, which proves a deviation from the behaviour of an ideal gas.

1.1.2. The Laws of Isobar and Isochrone Dilatability(Y.A.C. Charles-1787, Y.L. Gay Lussac).

At the modification of a state of a gas, at the variation of temperature, we may distinguish two aspects of this law:

p = K, the law of isobar dilatability
V =K, the law of isochrone dilatability.

Isobar dilatability law. At constant pressure, the volume of a gas increases for every degree of temperature with $\alpha = 1/273$ from the initial temperature. α coefficient is independent on the nature of the gas, on the temperature and on the pressure.

The mathematical expression of the law is :

$$V = V_0 (1+ \alpha t), \qquad \text{(relation 1)}$$

where: V_0 is the initial volume of the gas;
V – the volume of the gas at t degree;
$\alpha = 1/273 = 0.003667$;
$(1+ \alpha t)$ is the dilatation binomial of gases.

For a t_1 temperature, $t_1 > t$, the absolute growth of the volume is given by the difference V_1-V:

$$V_1 - V = V (t_1 - t) / 273, \qquad \text{(relation 2)}$$

And the relative variation of the volume is given by the ratio:

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$$V_1 / V = (273+t_1) / (273+t) \quad \text{or} \quad V_1 / V = T_1 / T, \quad \text{(relation 3)}$$

which exemplifies that at a constant pressure ,the volumes of two equal quantities of the same gas are proportional with the absolute temperature.

A particular form of the relation 3 is obtained by substituting the volume with density:

$$\rho_1 / \rho = T / T_1, \quad \text{(relation 4)}$$

which shows that the density of a gas is inversely proportional with the absolute temperature.

Isochrone dilatability law. At constant volume, the pressure of a gas increases , for each degree of temperature , with $\beta = 1/ 273$ of the initial pressure. The thermic coefficient of pressure ($\beta = 1/ 273 = 0.003667$), at constant volume, is equal to the dilatation coefficient in volume of the same gas.

The mathematical expression of the law is :

$$p = p_o (1+ \beta t), \quad \text{(relation 5)}$$

and the graphic representation of the law is similar to the preceding. The Charles- Gay Lussac is a limit law , meaning that the equality $\alpha = \beta$ is perfectly valid only for ideal gases.

For gases that are used in practice the values of the two coefficients are a bit different ; for example CO_2, where can reach 0.4%.

Case	$\alpha \bullet 10^{-7}$	$\beta \bullet 10^{-7}$
Hydrogen	36613	36600
Helium	36601	36582
Nitrogen	36644	36732
Case	$\alpha \bullet 10^{-7}$	$\beta \bullet 10^{-7}$
Carbon dioxide	37262	37414
Air	36750	36760

Table 1

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1.1.3. Dalton's Law (of partial pressures).

J. DALTON proved through partial pressure law that: in the case of a chemical mixture (that don't chemically react) ,the pressure is equal to the sum of the pressures that each composing gas would exert if it would have occupied alone the entire volume of the mixture ,at the same temperature. So, the total pressure of a mixture of gases is equal to the sum of the partial pressure of the composing gases.

Denoting p_1, p_2, p_3,..... as the partial pressures of the composing gases in a mixture, the total pressure of , p, of the mixture is:

$$p = p_1 + p_2 + p_3 + \ldots \ldots$$

Similarly, we can write a relation for the total volume V of a gaseous mixture with the partial volumes V_1, V_2, V_3 ..... :

$$V = V_1 + V_2 + V_3 + \ldots\ldots$$

For the first time the additivity law of partial volumes was verified by E. H. Amagat (1880-1898).

The partial pressure of each constituent of a gaseous mixture is proportional with the fraction of volume occupied by the constituent.

All component of a gaseous mixture act as if they were ideal gases. This is why, there can be applied the state equation of the ideal gases for every gas. Thus, for a gas with pressure p_1 and number of moles n_1:

$$p_1V = n_1RT.$$

Because of $n_1 + n_2 + n_3 + \ldots = n$, which is the total number of the mixture , the state equation of it is:

$pV = nRT$

meaning: $p_1 = n_1p / n$

For a gas with pressure p_2 we'll have: $p_2 = n_2 p / n$.

The fractions n_1/n, n_2/n etc. are named molar fractions of the respective gas. The molar fraction of a constituent from a mixture(gaseous, liquid, solid) is defined as the ratio between the number of moles of each constituent and the total number of moles. So, if we note with x the molar fraction, the above relation can be written:

$$p_1 = x_1p \ ; \ p_2 = x_2p \ ; \text{ etc.}$$

Similarly:

$$v_1 = x_1V \ ; \ v_2 = x_2V \ ; \text{etc.}$$

Thus, knowing the molar fraction of a constituent from a mixture of ideal gases we can compute the partial pressure(or the partial volume) of every constituent of the mixture: $x_1 = p_1/p = v_1/V$.

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1.1.4. Avogadro's Law .

In 1811, the Italian physician Amedeo Avogadro elaborated the hypothesis according to that the gaseous elements like hydrogen, chlorine, oxygen and nitrogen have bi-atomic molecules: H_2, Cl_2, O_2 and N_2.This hypothesis was experimentally verified and it is known under the name of the theory or the AVOGADRO'S law. It says that: equal volumes of different gases , in the same conditions of temperature and pressure, contain the same number of molecules .

With the help of this law there can be verified the law of constant volumes. Thus, when one volume of hydrogen combines with one volume of chlorine , the reaction takes place between n molecules of hydrogen and n molecules of chlorine. A molecule of hydrochloric acid is formed by one hydrogen atom and one chlorine atom and, this is why the combination of the hydrogen volume in which we find n molecules with the chlorine volume in which we find the same number of molecules it is represented like this:

$$nH_2 + nCl_2 = 2nHCl$$

By simplification we obtain:

$$H_2 + Cl_2 = 2HCl$$

Avogadro's law proves that, having the same number of molecules, the volumes of the gaseous elements which react must be equal. If for n molecules of hydrogen and chlorine corresponds one volume, for 2n molecules will correspond 2 volumes.

When one molecule of hydrogen combines with one molecules oh chlorine, two atoms of the first molecules actually combines with two atoms of the last molecule, and the result is two molecules of hydrochloric acid.

When two volumes of hydrogen combine with one volume of oxygen, the reaction takes place between two molecules (4 atoms) of hydrogen and one molecule (2 atoms) of oxygen, resulting two molecules of water in vapours state.

When three volumes of hydrogen combines with one volume of nitrogen, the reaction takes place between three molecules (6 atoms) of hydrogen and one molecules (2 atoms) of nitrogen, resulting two molecules of ammonia.

Consequently, gases are formed of molecules and, molecules of atoms. Only mono-atomic gases (He, Ne, Ar, Kr, Xe, Rn) and the vapours of some metals (Zn, Cd, Hg etc.) contain free atoms.

1.1.5. Relative Mass of Atoms and Molecules. AVOGADRO'S number.

In chemistry, the relative atomic masses and the relative molecular masses, that means the atomic masses, respectively the molecular ones, are used related to an atomic mass unity(amu).

Firstly, after DALTON's proposal, the mass of hydrogen atom was elected as atomic mass unity. Subsequently, chemists used as a.m.u 1/16 of the atomic mass of natural oxygen, mixture of isotopes. Only physicians used for their precise calculations 1/16 of the mass of isotope 16O. To eliminate this inconvenient it was chosen as a.m.u.1/12 of the mass of isotope ^{12}C, neglecting the difference between them.

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By the concept of relative mass of an element we understand the number that shows us how many times an atom is heavier than the atomic mass unity. Similarly, by molecular mass we understand the number that shows us how many times the molecule of a substance is heavier than the atomic mass unity.

AVOGADRO'S number (N) is defined as the number of carbon-12 atoms that are to be found in exactly 12 grams of corbon-12. Its value is about 0.60229 * 10sqr24

A mole of substance is defined as the quantity of the substance that contains a number of molecules equal to the Avogadro's number. Thus, a mole of water ,H2O, is the quantity of water that contains N molecules H_2O. The molecular weight of water (the sum between the atomic weights of the composing atoms :2*1.00797 + 1*15.9994) is 18.0153. From the definition of atomic weight and mole we reach the conclusion that a mole of water weights 18.0153 grams.

A mole of iodine atoms is equal to 126.9044 grams of iodine and a mole of iodine molecules(I_2) is equal to 253.8088 grams if iodine. The weight of a compound with a chemical formula is sometimes equal to the number of grams equal to the sum of the atomic weights, corresponding to that formula, whether this one exists or not. Thus, the molar weight of the liquid acetic acid, with the formula CH_3COOH (1), is taken as 60.05, although the liquid probably contains dimmers [double molecules, $(CH_3COOH)_2$].

1.1.6. State equation.

Boyle-Mariotte's law: pV=k, and Gay-Lussac's law: V/T=k' can be united in one single expression . We consider that the gas has the initial pressure po = 1 atm, To=273°K and the volume Vo.

If we maintain the pressure constant the gas warms up until it reaches the temperature T and the volume increases from Vo to V_t:

$$V_t = VoT/T_o. \qquad \text{(relation 1)}$$

Then, if we maintain the temperature constant ,T, and pressure varies from po to p, the volume passes from V_t to V:

$$poV_t = pV. \qquad \text{(relation 2)}$$

Using relation 1:

$$poVo / To=pV / T \qquad \text{(relation 3)}$$

In the left side of the relation we have only constant physical quantities and thus why the right part of the relation should also be constant:

$$pV / T=k \qquad \text{(relation 4)}$$

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Using relation 4 we deduct that at absolute zero (T = 0), pV must be zero, which means that p or V must be zero. V is always non-zero and this is why po=0. This situation would have been theoretically possible if the molecules of the gas would not manifest thermic agitation, which is impossible. Consequently, no gas can exist at absolute zero.

If we apply relation 4 to a mole of gas, which has a constant volume V (Avogadro's law), it results:

$$pV / T = R$$

The constant R is independent of the nature of gas and it is called the constant of ideal gases or the constant of gases. The expression:

$$pV = RT$$

is named the state equation of ideal gases.

If n gram-molecules of gas occupies the volume V then 1 mole of gas will occupy the volume V/n. We'll have the following state equation:

$$pV / n = RT \qquad \text{or} \qquad pV = nRT$$

The number of moles ,n, is equal to the ratio between the mass, m, of the gas (in grams) and the value of its molecular mass ,M, :

$$n = m / M.$$

Substituting in the above relation we'll obtain:

$$pV = mRT/M.$$

Constant's of gases value.

$$R = pV/ nT$$

It has the following dimensions:

R = [pressure] [volume] / [temp.] [no. of moles] =
= [force/aria] [volume] / [temp.] [no. of moles]
= [force] length] / [temp.] [no. of moles] = [energy] / [temp.] [no, of moles]
R = po Vo / 273 = 1 atm x 22.4 l / 273 = 0.082 l x atm/degree• mole
R = po Vo / 273 = 760 mm x 22400 ml / 273 = 62400 ml mm / degree• mole
R = 1.0132 x 10 x 22414 / 273 = 8.3143 x 10 erg / degree •mole
= 8.3143 J / degree•mole
R = 8.3143 / 4.1868 = 1.9872 cal. / degree•mole

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1.1.7. Mendeleev-Clapeyron's Equation (1874).

$pV = m\ RT/M$ is the complete form of Mendeleev-Clapeyron's equation and it is used for gases in other conditions than the normal ones.

The value of R doesn't depend on the nature or quantity of the gas but on the units of measure of pressure and volume. To understand the physical meaning of constant R, let's consider the relation $pVm = RT$. At a constant pressure and an increasing of temperature ΔT corresponds an increasing of volume (ΔVm) . So, we'll have the following equation:

$$p(Vm + \Delta Vm) = R(T + \Delta T) \quad \text{or}$$
$$pVm + p\Delta Vm = RT + R\Delta T$$

Using the initial condition we'll obtain:

$$p \bullet \Delta Vm = R\Delta T \quad \text{and } R = p \bullet \Delta Vm/\Delta T$$

The product between the pressure and volume's variation is the work (ΔA) , so :

$$R = \Delta A/ \Delta T.$$

If we consider $\Delta T = 1°C$ we'll obtain:

$$R = \Delta A.$$

Thus, the gaseous constant (R) represents the work of dilatation done by one mole of ideal gas when heating with 1°C, at constant pressure.

Mendeleev – Clapeyron's equation is used for computation of every physical quantity in the expression $pV = mRT/M$, when all others are given. Taking into account that $\rho = m/V$ it results:

$$\rho = pM/RT$$

which shows that the density is directly proportional with pressure and molecular mass and, inversely proportional with absolute temperature.

Mendeleev – Clapeyron 's equation leads to a conclusion also found at Avogadro's law. Thus, denoting ρ as the density of a gas and ρo the density of a reference gas, in the case of 2 gases we'll have:

$$\rho = pM/RT \quad \text{and} \quad \rho o = pMo/RT$$

The ratio $\rho/\rho o$ is the relative density of the gas in comparison to the reference one:

$$dr = \rho/\rho o = M/Mo.$$

This relation proves that the ratio of the densities of 2 gases is equal to the ratio of their molecular masses.

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1.2. Nonideal gases.

1.2.1. Deviations from the ideal gas laws.

From the state equation we know that pV=constant and that pV = RT for a mole of gas. Considering the pressure of 1 atm (and every temperature constant) pV/RT = 1, there are noticed considerable deviations at high pressures.

The value of the ratio pV/RT , called compressibility factor , varies at nonideal gases depending on temperature and pressure, having sub-unitary values at medium pressures and low temperatures and, super-unitary values at high pressures . (Table 2).

Variation of compressibility factor (the ratio pV/RT) with pressure

Pressure (atm)	H_2 (0°C)	N_2 (0°C)	CO_2 (40°C)
1	1,000	1,000	1,000
50	1,033	0,985	0,741
100	1,064	0,985	0,270
200	1,134	1,037	0,409
400	1,277	1,256	0,718
800	1,566	1,716	1,299

(Table 2)

The deviations from the ideal gas laws, at high pressures , depend on the nature of gas and they are of two types . At hydrogen (and helium) the ratio pV/RT increases continually with pressure; at nitrogen, carbon dioxide and other gases this ratio firstly decreases and , when the pressure is higher it increases back.

The curves of the different gases represented in a diagram, determined at a constant temperature , are called isothermic. Except hydrogen, the isothermics of every gas from the figure present a minimum , after which an almost linear increasing follows. The isothermics of hydrogen, at lower temperatures, presents a minimum similar to that of the other gases.

So, the minimum point in the isothermic of a gas depends on temperature. For every gas there is a temperature, called Boyle's temperature, above which the isothermic does not present a minimum anymore and the product pV is equal or greater than RT. The minimum point is more remarkable at low temperature, nearer to condensation temperature, at which the deviations from the ideal gas laws are the greatest.

The deviations from the ideal gas laws are caused by two antagonistic effects : an attraction between molecules (which is manifested through an abnormal decreasing of V) and a repulsion between molecules (which is visible from the increasing of p). Both effects are unexpected in the theory of ideal gases.

To make complete the image of the behaviour of a nonideal gas there are reproduced the deviations from Boyle-Mariotte's law (pV=constant) of the ammonia at isothermic compression in table 3. It will be noticed the sudden decreasing of volume at the pressure of condensation (liquefaction) of 9.8 atm.

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Measurements of pressure and volume at 17.00 g (1mole) ammonia, at 25°C

Pressure (atm)	Volume (litres)	PV
0.1	244.5	24.45
0.2	122.2	24.44
0.4	61.02	24.41
0.8	30.44	24.35
2	12.17	24.34
4	5.975	23.9
8	2.925	23.4
9.8	2.36	23.1
9.8	0.02	0.2
20	0.02	0.4
50	0.02	1

(Table 3)

24.45 gas
23.1 the beginning of condensation
the gas disappears; it's present only liquid
only liquid

1.2.2. I.D. van der Waals' equation.

The laws of ideal gases were deducted from the kinetic theory on the basis of the following statements: the volume of the molecules is negligible in comparison with the total volume of the gas; the molecules do not exert attraction between them.

Any gas that manifest deviation from the application of the state equation of ideal gases,

$$pV = nRT$$, is a real gas.

At nonideal gases, the volume occupied by a certain quantity of gas, at a defined pressure p and temperature T, is bigger than the one predicted by the law of the ideal gases. So, taking into account that $(pV)_{ideal} = nRT$, respectively $(pV)_{ideal}/nRT = 1$ and V_{real} is bigger than V_{ideal}, it results:

$$(pV)_{real} /nRT > 1$$

The pressure exerted by a certain quantity of real gas, at a defined temperature, is lower than the one indicated by the law of ideal gases. So, because p_{real} is lower than p_{ideal} , it results that:

$$(pV)_{real} /nRT < 1.$$

It can be exemplified deviations from the ideal gas laws of these gases. At hydrogen, the intermolecular attraction forces are weak and this is why they do not significantly influence pV; in exchange, the volume increases the values of pV over the ideal values. At nitrogen, the intermolecular attraction forces cause negative deviations of the values of pV at pressures of over 15 atm. At carbon dioxide, the intermolecular attractions are more intense at 40°C than those of the nitrogen at 0°C. Both for nitrogen and carbon dioxide there is a pressure (150, respectively 600 atm)

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when the product pV becomes ideal, because of the counterbalance of the two influences : molecular volume and intermolecular attraction.

For nonideal gases I.D van der Waals (1873) established a relation that represents a modification of the state equation of ideal gases, regarding pressure and volume:

$$(p + n^2a/V^2)(V - nb) = nRT$$

The term n^2a/V^2 is a correction that takes into account the intermolecular attraction forces. This correction acts as a pressure that condenses the gas. This is called internal pressure and its size is inversely proportional with the square of the volume. The term a is a constant of proportionality and characterises the property of mutual attraction of the gas molecules. The term b is also a constant and represents the correction that takes into account the actual volume of the molecules and the mutual repulsion between gas molecules. It is known as covolume and represents the smallest volume that can be realised at the compression of a gas (when the attraction and repulsion forces are equivalent). The covolume is aprox. equal to the 4 times the actual volume of the molecules.

Van der Waals' equation has limited validity; for exact computations it must be extended by introducing other factors .

At usual temperatures, the influence of the term n^2a/V^2 is dominant at low pressures, while the influence of the term b is dominant at high pressures.

At very low pressures, where V has great value, both n^2a/V^2 and b have small values in comparison with p, respectively with V; in this case, van der Waals' equation is reduced to state equation of ideal gases: pV = nRT. Consequently, in these conditions, all nonideal gases submit to the laws of ideal gases. Thus, these laws can be considered as representing the limited behaviour of gases at pressures infinite small.

The interpretation of this result, chemically based, is that at low pressures in the unit of volume there are very few molecules such that the attraction force between them can be negligible; the volume of the gas is so big that the volume of molecules is comparatively negligible. In consequence, the nonideal gas behaves as if it was created from molecules that do not mutually attract, equally to an ideal gas.

Values of a and b for several gases:

Gas	$a \cdot 10^{-6}$	B
H_2	0.245	26.6
He	0.03253	23.2
O_2	1.361	31.8
N_2	1.348	39.6
CO_2	3.6	42.8
H_2O	5.45	30.5

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1.2.3. Critical constants.

It was proved that in gaseous state the molecules of substances are relatively distant between each other and they are in continuous motion. This motion defeats the attraction force between molecules. Still, if the temperature decreases the kinetic energy of the molecules is so much reduced that the attraction forces can not be defeated anymore; the molecules attract one another and result a liquid. This process is called liquefaction or condensation and it can be favoured if the pressure of the gas increases (respectively the volume decreases). The temperature and pressure conditions at which the liquefaction is produced varies from one gas to another. For example, at air pressure, sulphur dioxide liquefies at -10°C, carbon dioxide at – 78.5°C, oxygen at -183°C. But, for example, sulphur dioxide can also be liquefied at 20°C if a pressure of 3.24 atm is applied.

In 1869, T. Andrews performed several thermic compression experiences of carbon dioxide and he obtained the curves p—V at different temperatures (figure 8). At 48.1°C, the curve is a parabola that corresponds to Boyle-Mariotte's law: pV = const. At 35.5 and 32.5°C several deviations are observed because the gas is more compressible. At 31.1°C, the curve manifests a modulation at 75 atm , after which, for a specific domain, it has a horizontal display. Under 31.1°C, every curve has three parts: the part towards right, which corresponds to the gas; the part from the middle, when both gas and liquid are present at the same temperature; the part towards left , which corresponds to the liquid.

Critical constants of some substance (Table 4)

Substance	Critical Temperature (°K)	Critical Temperature (°C)	Critical Pressure (atm)	Critical Molar Volume (cm^3)
He	5.3	-267.8	2.26	60
H_2	33.3	-239.8	12.8	68
N_2	126	-147	33.5	90
Ar	151	-122	48	75
O_2	155	-118	49.7	74
CO_2	304	31	73	95
Cl_2	417	144	76.1	124
NH_3	405	132	111.5	72
SO_2	427	154	77.7	125
H_2O	647	374	218.5	57

Such experiences proved that a gas can be liquefied through pressure only if its temperature is inferior to the so-called critical temperature.

The critical temperature of a gas, t_c, is the highest temperature at which the gas liquefies through the increasing of pressure.

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The critical pressure, p_c, is the pressure necessary to liquefy a gas at the critical temperature.

The critical volume, V_c, is the volume of 1 mole of gas at critical temperature and critical pressure.

The critical point is the modulation point on the critical isothermic corresponding to the critical temperature and pressure. At this point the substance is in a critical state. For example, for CO_2, the critical point corresponds to: p_c=73 atm, t_c=31.1°C and V_c=95 cm^3. At the critical point the liquid and the vapours become identical.

The existence of a critical state allows the differentiation of gases from vapours: it is considered gas the states of the substance above critical temperature and, vapours the states of the substance below critical temperature.

Knowing the critical state is very important. So, for a gas that can be liquefied , it must be under its critical temperature(over this temperature there is no liquefaction, whatever the pressure) . This explains why gases like: H_2, N_2, O_2, which have low critical temperatures (table 4), were considered as nonliquefactionable and called permanent gases. They are distinguished from gases like: CO_2, NH_3, SO_2, which can be liquefied at usual temperature, only through compression at a higher pressure than the critical one.

1.2.4. The Joule-Thomson effect.

Let's imagine a cylinder divided in two compartments by a piston. The left part of the cylinder is filled with a gas at a certain pressure and the right part is vacuumed. If the piston is set free it is displaced to the right because the gas tends to occupy entire volume of the cylinder. Still, the gas does not perform any work because the pressure that must be defeated is zero, so:

$$w = -p \bullet \Delta V = 0.$$

The experience was achieved through the work of J.P. Joule and W. Thomson (Lord Kelvin) in 1853 by introducing the cylinder in a calorimeter full of water. During relaxation, the temperature does not modify which shows that the gas did not replace the heat with the water from calorimeter, so: $\Delta E = q+w = 0$. It results that the internal energy of the gas does not depend on the volume that it occupies but only on the temperature.

The above affirmation (reporting on internal energy) is strictly valid only for the ideal gas' state. Nonideal gases behave differently. Between molecules of nonideal gases there are exerted two types of interactions: of attraction and of repulsion. This is why, when passing from a higher pressure to a lower one, or otherwise, a thermic effect appears, called Joule-Thomson effect. If the attraction forces are predominant, when passing from a higher pressure to a lower one, the gas gets cold (positive Joule-Thomson effect) and, if the repulsion forces are predominant the gas gets heated (negative Joule-Thomson effect).

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The Joule-Thomson effect was emphasised with the help of a device that allows a continuous leakage of the gas from pressure p_1 to pressure p_2 ($p_1 > p_2$) in a tube with insulating walls, through a tap or a porous cork.

Joule-Thomson experience corresponds to a process of constant enthalpy because of:

$$H_1 = E_1 + p_1V_1 = E_2 + p_2V_2.$$

It must be underlined the difference given the situation of a adiabatic process ($q = 0$), that corresponds to $\Delta E = w$, for which the relaxation of gases is always accompanied by a decreasing of temperature and the compression of gases – by an increasing of temperature.

Most gases present, at room temperature and not very high pressures, a positive Joule-Thomson effect. Still, in the same conditions, hydrogen and helium present a negative effect. Thus, H and He behave at room temperature in the same way as other gases at high temperatures. At lower temperatures H and He present a positive Joule-Thomson effect. So, for H and He , at room temperature, the repulsion forces are predominant and, for the other gases the attraction forces between molecules are predominant.

For each gas there is a temperature, called inversion temperature, T_I , at which the Joule-Thomson effect is inverted. Below T_I , the gas gets cold and above T_I, when relaxing, the gas gets heated.

In the field where van der Waals' equation is valid, the inversion temperature is aprox. double Boyle temperature. For example, at hydrogen the inversion temperature is 222°K and Boyle temperature is 109°K. At very high pressures, the inversion temperature is lower (closer to Boyle temperature).

1.2.5. Liquefaction of gases.

Some gases (like H_2, O_2, N_2) do not transform into liquids at the usual temperature, whatever the pressure. These are called permanent gases. Others (for eg. CO_2, SO_2, Cl_2, NH_3) liquefy at room temperature, by simple compression.

The isothermics of carbon dioxide at temperatures smaller than 31°C, for example the isothermic of 0°C, present a discontinuity at the pressure at which the liquefaction begins (point A in the figure 5). On AB fragment of the curve, the liquefaction progresses; there are present two phases, a gaseous and a liquid one. As much as the two phases coexist the pressure does not vary. In the point B there is no liquid CO_2. Increasing continuously the pressure the ratio pV/RT increases linearly.

The isothermics of carbon dioxide corresponding to temperatures over 31°C, for eg. The isothermic of 40°C, are similar to that of 0°C through the marked minimum, but at these temperatures the liquefaction can not be produced, whatever the pressure.

The gases of which the critical temperature is situated below usual temperature (aprox. 25°C) liquefy through a simple compression at a pressure superior to the critical one. If the critical temperature of gases is lower than the room temperature or

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than that of cooling water the so-called permanent gases do not liquefy through compression. For liquefaction of these gases the Joule-Thomson cooling effect is used.

The first method for liquefaction of air is based on this principle(Linde, 1896). The air is swept out by a compressor and it is compressed within a tube at 100-200 atm and then relaxed through a thin orifice, in a larger relaxation tube that surrounds the compression tube. The relaxed air , cooled off through Joule-Thomson effect , cools off the fresh air from the central tube. The device is thermally isolated and this is why the gas gets cold progressively until the liquefaction temperature is reached.

This method is technically based on an exchange of heat between the relaxed cooled off gas and the compressed one. In modern device there are used more efficient exchangers of heat but with a more complicated construction. Because of this improvement the initial pressure can be considerably diminished. One of these modern proceedings (according to Frank) condenses the initial air at only 5-6 atm. Another perfecting is that the relaxed gas , but still under pressure, is used in a turbine to produce work. Through this, it gets cold before to be reintroduced in the circuit. This kind of installations is completed with devices for moving off the impurities from air (CO_2, hydrocarbons) and with columns of distillation that separated the oxygen from nitrogen.

Linde method can not be applied for hydrogen and helium, which present at usual temperature a heating Joule-Thomson effect. To be liquefied through this kind of proceedings, these gases must be firstly cooled off below their inversion temperature. For liquefaction, hydrogen is firstly cooled off with liquid nitrogen (b.p -196°C = 77°K) . Helium may also be liquefied if it is firstly cooled off with liquid hydrogen (b.p. -257°C = 16°K). Helium has the smallest boiling point (4.2°K at pressure of 1 atm.).

VIII.2. **LIQUID STATE**.

INTRODUCTION

Liquids have their own volume but they do not have their own shape/form and take the shape of the vessel in which they find themselves, occupying a certain volume. The existence of a proper volume, the density which is greater than that of the gases, the slower diffusion, some liquids' viscosity etc prove that, at liquids, molecules are nearer than those of gases, the attraction forces manifest more intensely and they cause regions of systematic order of particles; still, these regions are temporary.

The properties of liquids considerably vary with temperature. Thus, at much inferior temperatures to the critic point there are differences between the properties of one substance in liquid state and those of the substance in a gaseous state. These differences become smaller in the proximity of the critical point. Similarly, in the proximity of the solidification point of a liquid there are manifested similitudes between the properties of the liquid and those of the solid.

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2.1. The vapour pressure of liquids.

2.1.1. Liquid-vapours equilibrium.

In the isothermic of a substance, at lower temperatures than the critical one, there is a section in which gas and liquid coexist, in which pressure remains constant. The pressure at which gas and liquid coexist, at a specific temperature, it is called vapours pressure of the liquid at that specific temperature. (By the term 'vapours' it is specified a gas below its critical temperature).

A liquid that partially fills a closed vessel is in equilibrium with its vapours. Those molecules of the liquid, which are animated by higher speeds than the medium one, abandon the liquid surface and pass in a vapours state. Inversely, the molecules from vapours phase, which come during the contact of their molecules with the liquid surface, return to liquid state. In equilibrium, the number of molecules, which are vaporise is equal to that of molecules which are liquefied. The vapours pressure remains constant(at constant temperature).

The vapours pressure is independent of vessel volume. If through one way or another the volume increases, a part of the liquid evaporates and the pressure does not change, as much as the liquid is still there. The vapours in equilibrium with the liquid are called saturated. So, at a given temperature, for each substance there exists a saturation pressure equal to the vapours pressure at that temperature. After the total evaporation of the liquid and if the volume is still increasing, the pressure diminishes below the vapours pressure of the liquid.

Many condensable substances are kept in steel cylinders, as liquids in equilibrium with their vapours. Their pressure remains practically constant until exhaustion, for example:

Substance	Cl_2	NH_3	SO_2	CO_2	CH_3Cl	CF_2Cl_2
Vapours pressure,atm	6.6	8.5	3.2	56.5	4.7	5.8 (at 20°C)

Permanent gases like H_2, O_2, N_2, are preserved compressed at high pressures (cca. 150 atm) in steel tubes; the pressure decreases continuously during the emptying.

2.1.2. Variation of vapours pressure in comparison with temperature.

One of these methods used for measurements of the liquids' vapours pressure consists of introducing a quantity of liquid within the empty space above the mercury column of a barometer. The difference between initial air pressure (for eg. 760 torr) and the measured height of the mercury column is equal to the vapours pressure of the liquid. In table 5, there are written the vapours pressures of water at different temperatures.

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Temperature		Pressure	Temperature		Pressure
°C	°K	(torr)	°C	°K	(atm)
-10	263	2.15	100	373	1.00
0	273	4.68	120	393	1.96
10	283	9.2	150	423	4.70
20	293	17.5	200	473	15.3
30	303	31.1	250	523	39.3
40	313	55.1	300	573	84.4
60	333	149.2	350	623	176.3
80	353	355.1	374	647	217.0
100	373	760.0	critical temp.	critical temp.	

Table 5

2.1.3. The boiling.

In table 5, to each pressure corresponds a temperature, the vaporisation temperature. It is called boiling point the temperature at which the vapours equals an indicated temperature (e.g. for water the pressure is 355 torr, the boiling point is 80°C). It is called normal boiling point the vaporisation temperature of liquid at the pressure of 760 torr =1 atm.

Obviously, the condensing temperature of the saturated vapours is equal to his boiling temperature at the same pressure, for any liquid.

Through boiling we usually understand the forming vapours bubble within the entire mass of the liquid , in conditions in which the vapours abandon the liquid as free to relax. They only have to defeat the air pressure or the pressure that exists in the vessel where the boiling takes place. If there are not gas bubbles, sometimes very small, the forming of bubbles in boiling liquid does not take place. The regular drinking water contains dissolved air. When heating , air's solubility in water decreases and small bubbles of air are separated. The vaporisation takes place on the surface of these bubbles that grow large and fill themselves with vapours until they abandon the liquid. Many times the forming of these bubbles begins from the vessel's walls that adsorb small quantities of gas.

If the liquid does not contain a dissolved gas and the walls of the gas doesn't contain a dissolved gas , the liquid can get heat at a temperature superior to the normal boiling one and it overheats (the deaired water can overheats until 120°C). When, for some reasons , there are formed vapours bubbles the boiling takes place violently; the heat accumulated in the liquid suddenly vaporises a part of liquid until the temperature decreases at normal boiling point (100°C for water).

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Temperature	Water	Ethylic alcohol	Acetone	Benzene
0	4.58	12.2	67.3	26.7
20	17.53	43.9	184.8	74.7
40	55.32	135.3	421.5	182.7
60	149.4	352.7	860.6	391.7
80	0	812.6	-	757.6
100	355.1	-	-	-
	0			
	760.0			

2.1.4. The vapours pressure of solutions. Raoult's Law.

If we denote vapours pressure of the pure solvent with p_0 and the one of solution with p, at the same temperature, then the difference p_0-p is the decrease of the vapours pressure; the ratio $(p_0-p)/p_0$, noted with $\Delta p/p_0$ it is called the relative decreasing of vapours pressure.

According to F. M. Raoult (1877) ,the relative decreasing of vapours pressure of a diluted solution is directly proportional with the molar fraction of the solute within solution; it is independent of temperature and the nature of solute.

If we denote n_1 the number of moles of the solvent and with n_2 – the number of moles of the solute Raoult's Law can be formulated likewise:

$$(p_0-p)/p_0=n_2/(n_1+n_2)$$

Raoult's Law can also be expressed in the following form denoting x_1 the molar fraction of the solvent and x_2 the molar fraction of the solute ($x_1+x_2=1$), the relative decreasing of vapours pressure:

$$(p_0-p)/p_0=x_2$$

can also be written:

$$p/p_0=1-x_2=x_1,$$

meaning: $p=x_1/p_0$ which signifies that the vapours pressure of a solution is equal to the product between the vapours pressure of the pure solvent and its molar fraction.

With Raoult's relation help there can be calculated:
the vapours pressure of a solution when we know its concentration and the vapours pressure of the pure solvent;
the molecular mass of the solute when we know the vapours pressure of the solution and of the pure solvent, the concentration and the molecular mass of the solvent. Thus, if in Raoult's relation there are substituted n_1 and n_2 values:

$$n_1=m_1/M_1 \text{ and } n_2=m_2/M_2$$

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where m_1 is the solvent mass of M_1 molecular mass and n_2 the solute mass of M_2 molecular mass, it results:

$$(p_0-p)/p_0=(m_2/M_2)/(m_1/M_1+m_2/M_2).$$

2.2. Heat of vaporisation.

Under constant pressure, the liquids vaporise at constant temperature although the vaporisation of liquid consumes heat. Water, for example, if it is heated within an open vessel at air pressure begins to boil at 100°C. Water's and vapours' temperature remains 100°c until the last drop of water disappears then, if the heat supply continues the vapours get heated over this temperature.

The quantity of heat, in calories, consumed at the vaporisation of 1 gram of substance at constant temperature is called vaporisation latent heat, l_v. The heat consumed at the vaporisation of 1 mole of substance in the same conditions is called molar vaporisation latent heat,L_v. So, $l_v \bullet M=L_v$ (where M is the molecular mass). From the table we can observe that water has a vaporisation heat exceptionally high. This happens because the water molecules are united through hydrogen bonds, stronger than van der Waals bonds, that connect the molecules of nonpolar liquids.

Vaporisation heats of some liquids at boiling points, at 1 atm. pressure

Substance	L_v cal•g^{-1}	L_v cal•mol^{-1}	Substance	l_v cal•g^{-1}	L_v cal•mol^{-1}
Hydrogen	112	225	Water	540	9729
Oxygen	50	1630	Ethylic	208	9560
Nitrogen	47	1320	alcohol	86	6380
Chlorine	69	4878	Ethylic ether	94	7350
Carbon	86	3880	Benzene	59	7080
dioxide	71	14200	Chloroform		
Mercury					

Trouton's Law.

For many substances , the ratio between molar vaporisation heat and absolute boiling temperature is a constant:

$$L_v/T_f = 21.5$$

According to the definition($\int dS=\Delta S=S_2-S_1=\int \frac{\delta \cdot q_{rev.}}{T}=\frac{1}{T}\int \delta \cdot q_{rev.}=\frac{\Delta H}{T}$ this ratio is identical to the vaporisation entropy. The experience exerted by numerous substances showed that Trouton's law is applied only for liquids whose molecules are united through van der Waals bonds. It is not applied, for example, for water(L_v/T_f= 26) or alcohol whose molecules are associated through hydrogen bonds. This inapplication of Trouton's law is a clue that molecules of a liquid are associated , meaning they are united through stronger forces than van der Waals forces.

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2.3 Superficial tension of liquids

Within liquids the distance between molecules is small and the sphere of action of intermolecular forces is of order 10^{-6} cm.

If a molecule is within a field of intermolecular actions it is attracted equally in all directions of the attraction forces exerted by surrounding molecules such that the resultant force is practically null. If a molecule finds itself at the surface of liquid it is much more attracted by liquid's molecules than by gas molecules because these ones are in a smaller quantity; consequently, the resultant of the attraction forces is pointed towards the interior. If a molecule finds itself in nearness of the surface of separation gas-liquid but at a smaller distance than the radius of action sphere of the inter-molecular forces it is attracted towards the interior of liquid. The force with which a unit from the superficial layer of a liquid is attracted towards the interior of liquid represents the internal pressure for molecular pressure.

The internal pressure is quite high (it is higher than the pressure that could be exerted in the exterior in order to see the compression of liquid).

The existence of internal pressure is the cause of which liquids compress so difficult.

As a consequence of the attraction of molecules towards the interior of liquid, the liquid's surface is the subject of some uncompensated forces that acts perpendicular to the surface. So, the superficial layer of liquid can be imagined as acting like an elastic membrane, which tends to contract itself. The force that tends to decrease the surface of a liquid is called superficial tension. It represents force, measured in dyne, which acts on a fragment of 1 cm length, in tangential sense at the surface.

Usually, it is considered to be a superficial tension the force which exists at the interface between a liquid and its vapours or between a liquid and air. Still, there can also be manifested forces at the surface of separation between two miscible liquids or between a solid and a liquid. Such forces – interfacial tensions- have values that depend on the nature of interface.

The tendency of a liquid to contract is a consequence of the existence of free superficial energy; the transition towards the equilibrium state is accompanied by a decrease of free superficial energy. This tendency is described as the superficial tension, σ, meaning the force, in dyne, which acts tangential to the surface of a liquid on a straight line with a length of 1 cm. The free superficial energy and the superficial tension are numerically and dimensionally equal.

Superficial tension of liquids differentiate depending on their nature (molar volume, polarity of molecules, the property to create hydrogen bonds), meaning on the size cohesion forces of the liquid and so, on the size of internal pressure (table 8).

Superficial tensions, in $mN \bullet m^{-1}$, in comparison with air, at 20°C

Substance	σ	Substance	σ
Water	72.75	Benzene	28.9
Mercury	475	Ethylic alcohol	22.55
Carbon Sulphyde	32.4	Acetic acid	27.7
CCl_4	26.8	Nitrobenzene	43.55

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Still, when two unmiscible liquids come into contact, then the superficial tension decreases because to the cohesion forces oppose the attraction forces between those species of molecules. The forces that act at the surface of separation between two unmiscible liquids (or very little miscible) is called interfacial tension.(table 9).

Interfacial tensions, in $mN \bullet m^{-1}$, of some liquids, in comparison with water, at 20°C

Substance	σ	substance	σ
Mercury	375	Carbon sulphide	38.3
Benzene	34.9	CCl_4	45.1
Chloroform	27.7	Ethylic ether	9.7

The grater the molecular attraction between liquids the lower the interfacial tension; so, the miscibility of the liquids is greater. Thus, benzene dissolves very little in water; the ethylic ether dissolves better. When the attraction forces compensate the cohesion forces of one of the liquids then the liquids that form the two phases are miscible in any proportion, for example the system water- ethylic alcohol.
For comparison, superficial tensions can be expressed as molar superficial tensions ,σ_M, as referring to the surfaces that contain the same number of molecules:

$$\sigma_M = \sigma V^{2/3}$$

where V is the molar volume (occupied by N molecules).

Superficial tension decreases in the same time with the increasing of temperature because of, as temperature increases the kinetic energy of molecules also increases which displays a weakening of cohesion forces and a greater possibility for molecules to reach the surface of liquid; at critical temperature the superficial tension of liquids is null. This results from the relation

$$\sigma_M = k\sigma(T_K^{'} - T)$$

where: $T_K^{'}$ represents a temperature immediately below critical temperature, $k\sigma$ is a constant. The value of this constant is $2,1 erg \bullet degree^{-1}$ (respectively $2,1 \bullet 10^{-7}$ J $\bullet degree^{-1}$).

Superficial tension of solutions

In the case of liquid solutions their superficial tension depends on the nature of the solvent, on temperature and on the other limitrophe phase and on the nature and concentration of the dissolved substance.

At dissolution there are possible three cases: denoting σ as the superficial tension of solution and σ_0 – the superficial tension of pure solvent, there are considered:

$\sigma = \sigma_0$, the dissolved substance doesn't modify the superficial tension of solvent;

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$\sigma > \sigma_0$, the dissolved substance increases the superficial tension of solvent;

$\sigma < \sigma_0$, the dissolved substance decreases the superficial tension of solvent;

In the first two cases the dissolved substance are called inactive superficial substances or capillary-inactive and in the third case – active superficial substances or capillary active. Most electrolytes are superficial inactive substances.

The solutions of polar organic substances behave as superficial active substances (for example oils, fat acids, esters (Table 10).

Substance (18°C)	σ	Substance (15°C)	σ
10% H_2SO_4	74.1	0.5m Ethylic acetate	41.5
10% NaOH	77.3	0.5m Acetic acid	63.3
10% NaCl	75.51	0.5m Acetone	59.4
10% Na_2SO_4	75.15	0.5m Methanol	68.4
10% NH_4Cl	74.5	0.5m Propionic acid	54.1

2.4 Viscosity

Viscosity of liquids is the resistance opposed by the liquid to the displacement of one of its layers in comparison with another.

Let's suppose that a layer of liquid, B, moves in comparison with another layer of liquid, A, considered at rest, with a velocity v(figure 11) . If the distance between the mobile layer B and the rest layer A is l and the surface of contact between the two layers is s, the force F which appears between the two layers (internal friction) is proportional to the surface contact s and to the displacement speed of the mobile layer B and it is inversely proportional with the distance l between layers:

$$F=\eta sv/l$$

It is called viscosity coefficient or viscosity the coefficient of proportionality η.

From this relation it results that the dimensions of viscosity are mass/length x t(g/cm.s). The unit of measure of viscosity coefficient is named poise(P) and represents the friction force when the distance between layers is of 1 cm, the contact surface is $1cm^2$ and the speed of displacement of one layer to another is 1 cm/s. Practically, it is used a submultiple of 100 times smaller , called centipoise (cP).

The coefficient of viscosity is also titled as dynamic viscosity. Kinematics viscosity is defined as the ratio between the dynamic viscosity and the liquid's density: $\nu = \eta/\rho$,

and its unit of measure is named stockes (St).

In industrial labs it is used as conventional unit of measuring viscosity Engler degree.

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Engler viscosity, E, of a liquid is the ratio between passing time, t_1(expressed in seconds) of 200 ml liquid through standardized orifice at a certain temperature and the passing time t_0 of 200 ml water at 20°C:

$$°E=t_1/t_0.$$

The ratio t_1/t_0 is expressed in Engler degrees (°E), indicating the temperature, as index, at which the leakage of liquid is made(e.g. $°E_{50}$- was determined at 50°C)

The viscosity of a liquid generally decreases at the same time with the increasing of temperature.

VIII.3. **SOLID STATE. CRYSTALS**

Crystalline and Amorphous Substances

Most solids are crystalline in structure, but there are solid substances (glass, pitch, glue, etc.) whose fracture gives no indications of crystals and they are called amorphous.

Each crystalline substance usually gives crystals of quite definite form. The classification of crystalline forms is based on determination of the degree of symmetry of crystals.

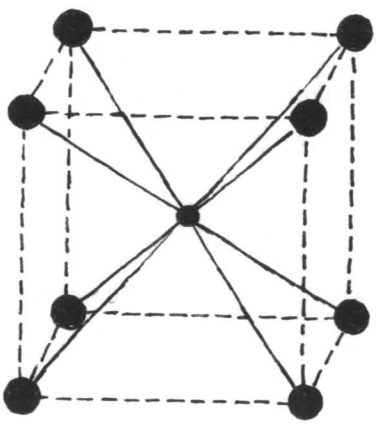
The structure of solids can be described as if they were three–dimensional analogs of a piece of wallpaper. Wallpaper has a regular repeating design that extends from one edge to the other. Crystals have a similar repeating design, but in this case the design extends in three dimensions from one edge of the solid to the other.

We can unambiguously describe a piece of wallpaper by specifying the size, shape and contents of the simplest repeating unit in the design. We can describe a three–dimensional crystal by specifying the size, shape and contents of the simplest repeating unit and the way these repeating units stack to form the crystal.

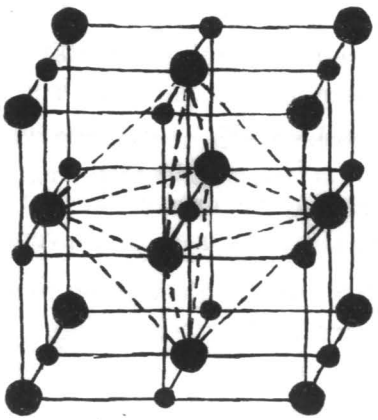
The simplest repeating unit in a crystal is called a unit cell. Each unit cell is defined in terms of lattice points – the points in space about which the particles are free to vibrate in a crystal.

The structures of the unit cell for a variety of salts are shown below.

CsCl



NaCl



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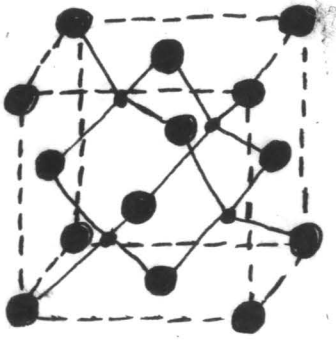
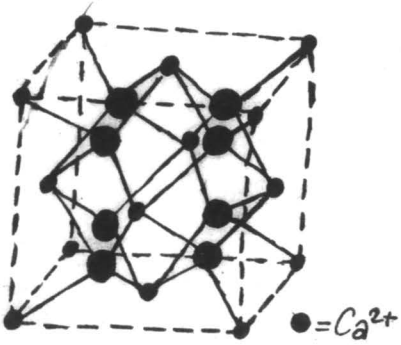
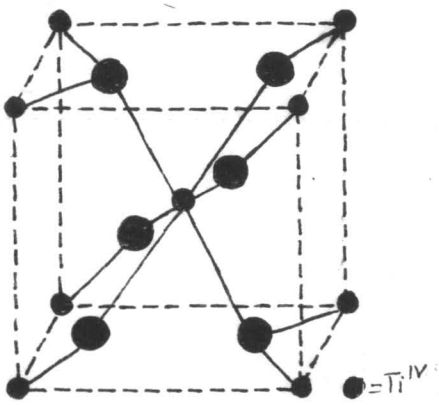
Zinc blende (cubic ZnS)



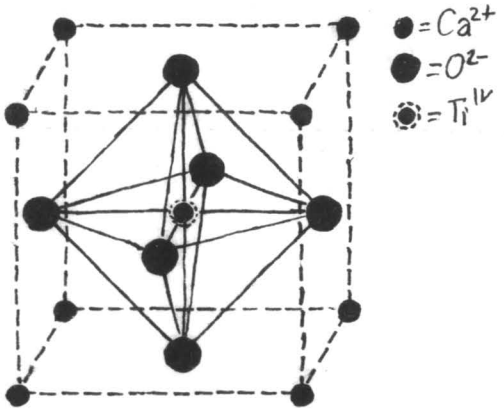
Fluorite (CaF_2)



Rutile (TiO_2)



Perovskite ($CaTiO_3$)

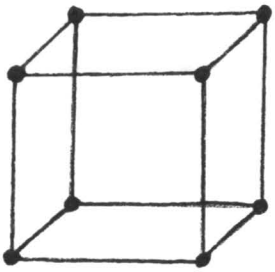


In 1850, Auguste Bravais shoed that crystals could be divided into 14 unit cells, which meet the following conditions:

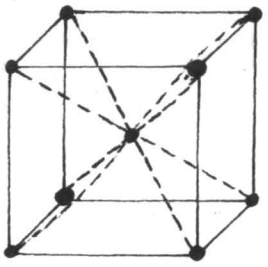
- The unit cell is the simplest repeating unit in the crystal.
- Opposite faces of a unit are parallel.
- The edge of the unit cell connects equivalent points.

The 14 Bravais unit cells are shown in the figure below.

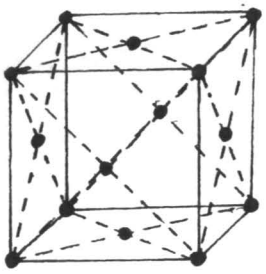
Cubic



Simple



Body–centered



Face centered

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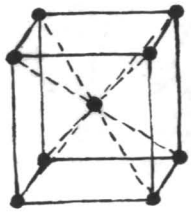
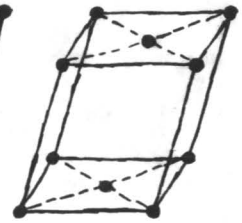
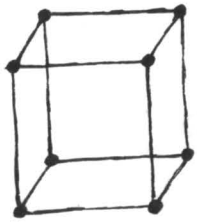
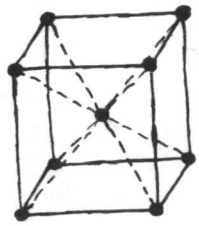
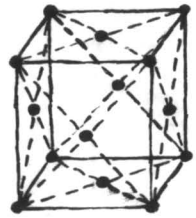
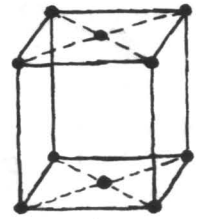
Tetragonal Monoclinic



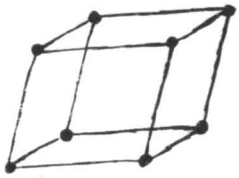
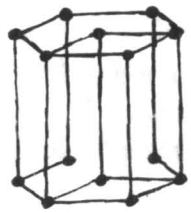
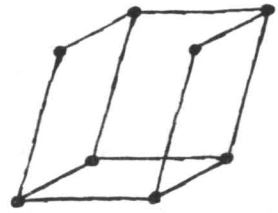


Simple Body–centered Simple End–centered
Orthorhombic

Simple Body–centered Face centered End centered

Rhombohedral Hexagonal Triclinic

These unit cells fall into seven categories, which differ in the three unit–cell edge lengths (a, b and c) and three internal angles (α, β and γ) as shown in the table below.

The Seven Categories of Bravais Unit Cells:

Category	Edge Lengths	Internal Angles
Cubic	$(a = b = c)$	$(\alpha = \beta = \gamma = 90^0)$
Tetragonal	$(a = b \neq c)$	$(\alpha = \beta = \gamma = 90^0)$
Monoclinic	$(a \neq b \neq c)$	$(\alpha = \beta = 90^0 \neq \gamma)$
Orthorhombic	$(a \neq b \neq c)$	$(\alpha = \beta = \gamma = 90^0)$
Rhombohedral	$(a = b = c)$	$(\alpha = \beta = \gamma \neq 90^0)$
Hexagonal	$(a = b \neq c)$	$(\alpha = \beta = 90^0, \gamma = 120^0)$
Triclinic	$(a \neq b \neq c)$	$(\alpha \neq \beta \neq \gamma \neq 90^0)$

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The most important unit cell category is the cubic one. A number of metals, ionic solids and intermetallic compounds crystallize in cubic unit cells. It is relatively easy to do calculations with these unit cells because the cell–edge lengths are all the same and the cell angles are all 90^0.

The simple cubic unit cell is the simplest repeating unit in a simple cubic structure. Each corner of the unit cell is defined by a lattice point at which an atom, ion or molecule can be found in the crystal. By convention, the edge of a unit cell always connects equivalent points. Each of the eight corners of the unit cell therefore must contain an identical particle. Other particles can be present on the edges or faces of the unit cell, or within the body of the unit cell. But the minimum that must be present for the unit cell to be classified as simple cubic is eight equivalent particles on the eight corners.

The body–centred cubic unit cell is the simplest repeating unit in a body–centred cubic structure. Once again, there are eight identical particles on the eight corners of the unit cell. However, this time there is a ninth identical particle in the center of the body of the unit cell.

The face–centred cubic unit cell also starts with identical particles on the eight corners of the cube. But this structure also contains the same particles in the centers of the six faces of the unit cell, for a total of 14 identical lattice points. The face–centred cubic unit cell is the simplest repeating unit in a cubic closest–packed structure. In fact, the presence of face–centred cubic unit cells in this structure explains why the structure is known as cubic.

Natural crystals, as well as crystals obtained by artificial means, rarely correspond exactly to the forms shown. When a solid substance is crystallized out of solution the result is also mostly irregular crystals, distorted due to nonuniform growth during crystallization, but no matter how its shape is distorted, the angle between the faces of a crystal of any definite substance is always constant. This is the "Law of Constancy of Interfacial Angles".

In many crystals, the difference between the cohesion in various directions is so great when struck or broken, they split along planes perpendicular to these in which the cohesion is the smallest. This property is called cleavage.

The difference between crystalline and amorphous substances is especially pronounced in their attitude towards heating. Amorphous substances have no clear cut melting point. The internal structure of amorphous substances is also similar to that of liquids. It is characterized by an unordered arrangement of its molecules. Only crystalline substances are considered solids.

It can be observed the fact that one and the same substance may be both crystalline and amorphous, depending on the conditions under which it passes into the solid state. For example, if glass is repeatedly heated and cooled slowly, it passes from the amorphous to crystalline state.

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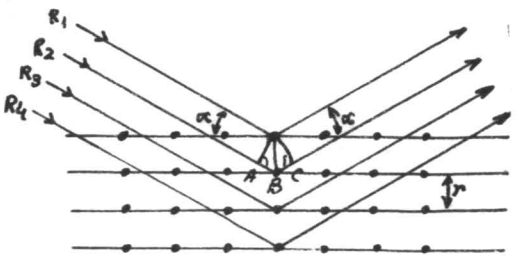
3.1. *The Atom in a Crystal. X–ray Diffraction in Crystals.*

It is well known the fact that the light suffers diffraction when it passes very small openings in a metallic plate or when is reflected by a metallic surface that has drown a network of parallel, closed lines. These diffracted waves interfere and produce (if it is used a monochromic light) interference fringes which are a system of dark and bright threads. For the interference to occur, the network constant must be smaller then $\lambda/2$. Between the network constant (distance between the network lines, r) and the wave length of light, λ, is a direct relationship.

Since their discovery (by Roentgen, 1895), it was proposed the fact that the X–rays are transversal electromagnetic vibrations having the same nature as the light, but of smaller wave length. In 1912, Laue proposed the use of crystals as networks supposing that the distance between atoms in crystals must be of the same order of measurement as the wave lengths of the X–rays.

When a narrow X–ray beam gets on a crystal, most of the rays pass the crystal, some suffer diffraction and produce, on a photographic plate, spots of different intensities, symmetric placed round a most intense, central spot that is produced by the undiffracted rays.

W. Bragg proposed, in 1912, a method to analyze the structure of crystals with the help of X–rays. It was used a monochromic X–ray (of the single wave length λ) obtained by the use of a confineable anticatode. In the figure bellow, it is shown the interference of X–rays at the reflection on the planes of a crystalline network:



Bragg is the same who developed the X–rays diffraction through crystal theory.

It can be proved that the X–rays diffraction after passing a crystal is the same as their reflection on parallel atom planes of the crystal. Like for the usual reflection, the incidence angle is equal to the reflection one. Unlike the usual reflection, X–ray diffraction takes place only then when the incidence angle has certain values. It was obtained the relation (the Bragg law):

$$2r \sin \alpha = n \lambda$$

A widely used method to analyze the crystals by X–rays is the rotating crystal method (Polanyi, 1920). It is used the apparatus shown in the figure:

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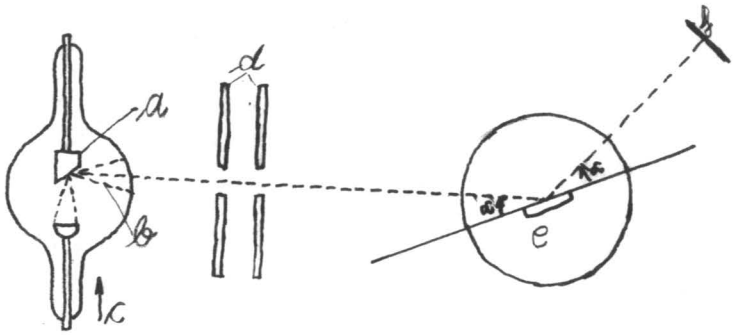

a)–anticatod; b)– X–rays; c)– electrons; d)– screens; e)– crystal; f)– detector.

A beam of X–rays emitted by the anticatode is made parallel by the passing of holes of more then one screens, is reflected by the crystal which is rotating around a crystallographic axis. There are produced images on the detector (photographic film or detector of ionization) only for the positions when the angle α corresponds to the Bragg law.

3.2. The Structure of Spatial Lattices

Spatial Lattices

It was proposed the regular form of crystals as a perfect ordered construction of tiny particles (Hauy, 1781; Bravais, 1848).

It is known the fact that a crystal is made of a succession of planes in which their points are occupied by the component particles of the crystal (atoms, ions or molecules). This construction is called a spatial lattice. The simplest part of a spatial network is called unit cell. A spatial lattice is composed by a succession of unit cells, identical and infinitely repeating (without empty spaces between them).

An unit cell is perfectly defined when there are known the number and the position of composing particles (atoms, ions and molecules), the lengths of the three edge lengths and the internal angles.

Measuring the Distance between Particles

Nickel is one of the metals that crystallize in a cubic closest–packed structure. When you consider that a nickel atom has a mass of only 9.75×10^{-10} m, it is a remarkable achievement to be able to describe the structure of this metal. The obvious question is: how do we know that nickel packs in a cubic closest–packed structure?

The only way to determine the structure of matter on an atomic scale is to use a probe that is even smaller. One of the most useful probes for studying matter on this scale is electromagnetic radiation.

In 1912, Max van Laue found that X–rays that struck the surface of a crystal were diffracted into patterns that resembled the patterns produced when light passes through very narrow slit. Shortly thereafter, William Lawrence Bragg, who was just

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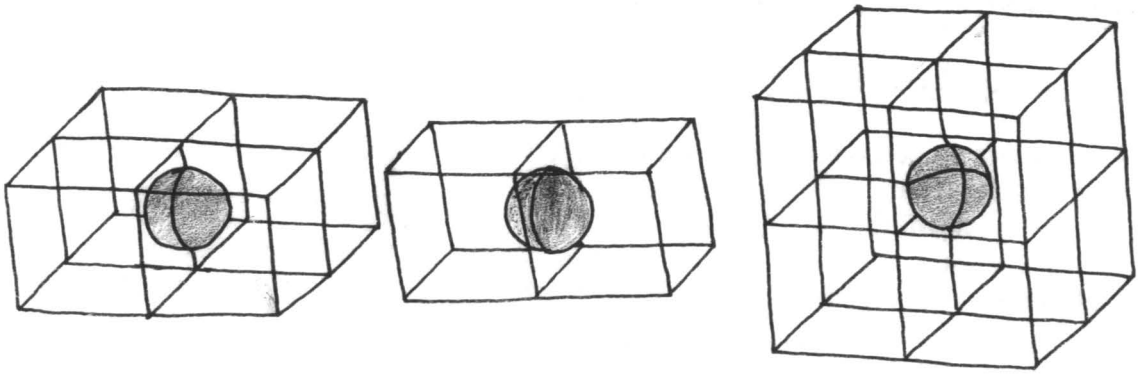
completing his undergraduate degree in physics at Cambridge, explained van Laue's results with an equation known as the Bragg equation, which allows us to calculate the distance between planes of atoms in a crystal from the pattern of diffraction of X–rays of known wavelength.

$$n\lambda = 2d \sin T$$

The pattern by which X–rays are diffracted by nickel metal suggests that this metal packs in a cubic unit cell with a distance between planes of atoms of 0.3524 nm. Thus, the cell edge length in this crystal must be 0.3524 nm. Knowing that nickel crystallizes in a cubic unit cell is not enough. We still have to decide whether it is a simple cubic, body–centred cubic or face–centred cubic unit cell. This can be done by measuring the density of the metal.

Determining the Unit Cell of a Crystal

Atoms on the corners, edges and faces of a unit cell are shared by more than one unit cell, as shown in figure below.



An atom on a face is sheared by two cells, so only half of the atom belongs to each of these cells. An atom on an edge is sheared by four unit cells and an atom on a corner is sheared by eight unit cells. Thus, only one quarter of an atom on an edge and one–eight of an atom on a corner can be assigned to each of the unit cells that share these atoms.

If nickel crystallizes in a simple cubic unit cell, there would be a nickel atom on each of the eight corners of the cell. Because only one eight of these atoms can be assigned to a given unit cell, each unit cell in a simple cubic structure would have one net nickel atom.

Simple cubic structure:

8 corners × 1/8 = 1 atom

If nickel formed a body–centred cubic structure, there would be two atoms per unit cell, because the nickel atom in the center of the body wouldn't be sheared with any other unit cell.

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Body–centered cubic structure:

$$(8 \text{ corners} \times 1/8) + 1 \text{ body} = 2 \text{ atoms}$$

If nickel crystallizes in a face–centred cubic structure, the six atoms on the faces of the unit cell would contribute three net nickel atoms, for a total of four atoms per unit cell.

Face–centred cubic structure:

$$(8 \text{ corners} \times 1/8) + (6 \text{ faces} \times 1/2) = 4 \text{ atoms.}$$

Because they have different numbers of atoms in a unit cell, each of these structures would have a different density. Let's therefore calculate the density for nickel based on each of these structures and the unit cell edge length for nickel given: 0.3524 nm. In order to do this, we need to know the volume of the unit cell in cubic centimeters and the mass of a single nickel atom.

The volume (V) of the unit cell is equal to the cell–edge length (a) cubed:

$$V = a^3 = (0.3524 \text{ nm})^3 = 0.04376 \text{ nm}^3$$

Since there are 10^9 nm in a meter and 100 cm in a meter, there must be 10^7 nm in a cm.

$$\frac{10^9}{1 \text{ m}} = \frac{1 \text{ m}}{100 \text{ cm}} = 10^7 \text{ nm/cm}$$

We can therefore convert the volume of the unit cell to cm^3 as follows:

$$4.376 \times 10^{-2} \text{ nm}^3 \times \left[\frac{1 \text{ cm}}{10^7 \text{ nm}}\right]^3 = 4.376 \times 10^{-23} \text{ cm}^3$$

The mass of a nickel atom can be calculated from the atomic weight of this metal and Avogadro's number:

$$\frac{58.69 \text{ g Ni}}{1 \text{ mol}} = \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 9.746 \times 10^{-23} \text{ g/atom}$$

The density of nickel, if it crystallizes in a simple cubic structure, would therefore be 2.23 g/cm^3, to three significant figures.

Simple cubic structure:

$$\frac{9.746 \times 10^{-23} \text{ g/unit cell}}{4.376 \times 10^{-23} \text{ cm}^3\text{/unit cell}} = 2.23 \text{ g/cm}^3$$

Because there would be twice as many atoms per unit cell if nickel crystallized in a body–centered cubic structure, the density of nickel in this structure be twice as large.

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Body–centered cubic structure:

$$\frac{2\ (9.746 \times 10^{-23})\ \text{g/unit cell}}{4.376 \times 10^{-23}\ \text{cm}^3\text{/unit cell}} = 4.45\ \text{g/cm}^3$$

There would be four atoms per unit cell in a face–centered cubic structure and the density of nickel in this structure would be four times as large.

Face–centered cubic structure:

$$\frac{3\ (9.746 \times 10^{-23})\ \text{g/unit cell}}{4.376 \times 10^{-23}\ \text{cm}^3\text{/unit cell}} = 8.91\ \text{g/cm}^3$$

The experimental value for the density of nickel is 8.90 g/cm^3. The obvious conclusion is that nickel crystallizes in a face–ccentred cubic unit cell and therefore has a cubic closest–packed structure.

Compact Lattices

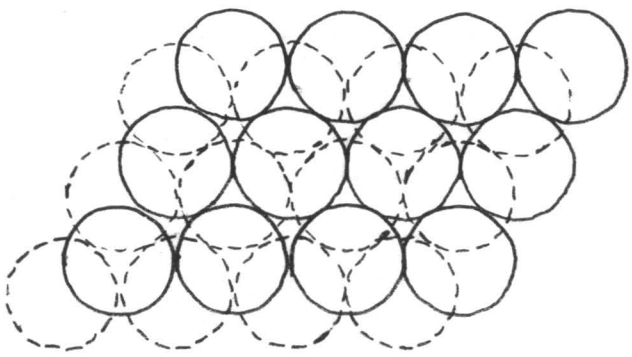
It is considered the fact that the form of atoms and monoatomic ions is a sphere. The rays are different for different atoms. The atoms that are attracted by nonorientated forces (ionic bonds, metallic bonds or van der Waals forces) have the tendency to form compact lattices, to occupy as much as possible the free space.

Compact arrangements of equal spheres.

A closed packing of spheres involves superimposing, one over another, of close layers (planes).

In a bidimensional arrangement, six spheres can surround each sphere. In the case when a sphere is surrounded by six spheres in a hexagonal arrangement, it results a more compact structure, with trigonal holes.

Six spheres surround one sphere: if is placed a second layer of spheres, when one sphere is placed in the hole left by three spheres in the bottom (see the figure below).



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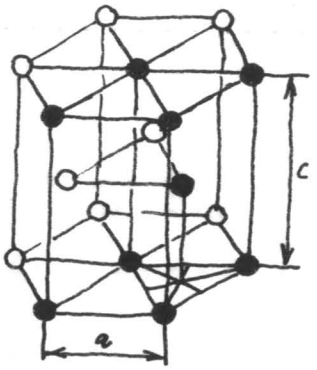
A third layer can be placed, but in two different ways:

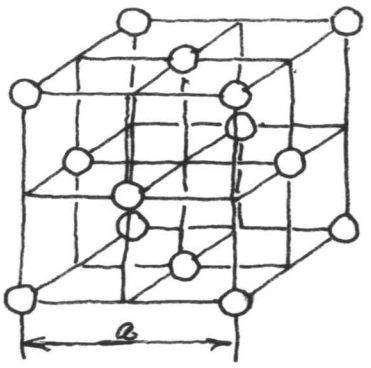
a)– the spheres of the third layer can be placed in the holes of the second layer that superpose the spheres of the first layer. So, the third layer is identical to the first one and the second layer would be identical with the fourth one and so on. This kind of succession of layers has a hexagonal symmetry and it corresponds to a hexagonal compact lattice shown in the figure below (a).

b)– the spheres of the third layer can also be placed in the holes of the second layer that superpose the holes of the first layer. In this arrangement, it results three different layers and only the fourth is identical with the first, the fifth is identical with the second and so on. This kind of succession gives a cubic compact lattice and it is shown in the figure below (b).

(a) hexagonal compact structure.
Example: Magnesium.
a= 3.22 Å; c= 5.23 Å.



(b) cubic compact structure.
Example: Argon.
a= 5.42 Å.



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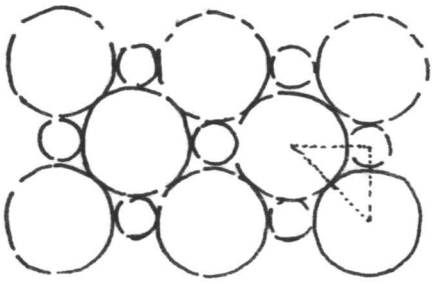
In both structures of equal spheres, 74.05 % of the space of the total volume of the crystal is filled with spheres. Each sphere is surrounded by 12 identical spheres (C.N. = 12). This is the maximum number of spheres that can touch one sphere in any arrangement. Compact structures of atoms with equal rays can be found at metals.

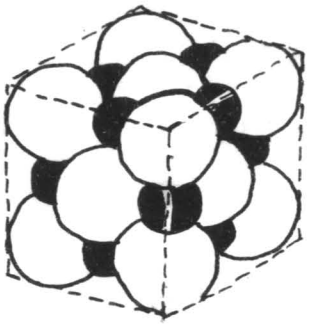
Arrangements of unequal spheres.

This is the case of the crystal composed by atoms with unequal rays. The type of the lattice is determined by the ratio between the cation and anion radii. For instance, in the NaCl structure, the ratio between the rays of the cation of sodium and the anion of chlorine is $r_c/r_a = 0.52$. Both ions have the coordination numbers of 6. Each ion of sodium is surrounded by an octahedral of chlorine ions and each chlorine ion is surrounded by an octahedral of sodium ions. This leads to the lattice of NaCl. In the figure below it is drown a part of NaCl crystal (c) and a three dimensional arrangement of NaCl. It can be observed that the Cl ions are bigger and form a cubic compact lattice and the Na ions are small and fill the holes of the lattice.

(c) a part of NaCl structure.
Na ions do not touch each other, but four Cl ions.



(d) The crystalline lattice of NaCl.
The big spheres are the Cl^- and the small ones are Na^+.



In the lattice of CsX (X = Cl or I), the ions have the coordination number 8. For α–CsCl: $r_c/r_a = 0.93$; CsI: $r_c/r_a = 0.78$.

The condition the ionic lattice to be stable is that the ions of opposite charge to touch.

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Types of crystalline lattices

The arrangement of the Particles in a lattice is given by the crystalline system. The crystalline lattices can be described regarding the nature of the particles and the nature of the bonds between particles. These are the following types of lattices:

1. atomic lattices (atoms) held together by the covalent bonds;
2. ionic lattices (ions) with Colombian interactions between atoms;
3. molecular lattices (molecules) held together by van der Waals forces;
4. layer lattices;
5. metallic lattices (metallic atoms) with metallic bonds.

1.Atomic Lattices

The arrangement of atoms has a given angles between atoms and no compact structure can be released. In many cases, the bond angle depends on the hybridization type: $-sp^3$ a tetrahedral arrangement is possible with σ bonds and $109^0\ 28'$ angle

example: C (diamond), Si, grey Ge, ZnS (blende) — f.c.c.; C.N. = 4.

$-sp^3d^2$ an octahedral arrangement: SF_6 or $[SiF_6]^{2-}$, $[AlF_6]^{3-}$.

The atomic crystal is a big molecule with covalent bond between atoms.

For the AB type of atomic lattices, the sum of electrons is equal to eight, the coordination number is 4 and the unit cell is face centered cubic.

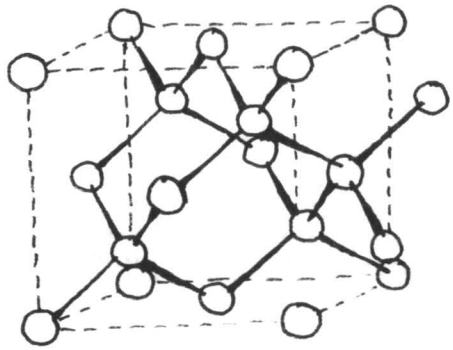
ZnS	ZnSe	ZnO	CdS	2 + 6 = 8
AlSb	GaSb	AlN		3 + 5 = 8
CuBr				1 + 7 = 8
SiC				4 + 4 = 8

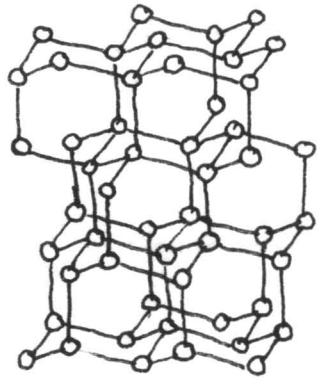
There are cases where the number of electrons is greater then eight: NiAs, PtSb and they are semiconductors.

For the AB_2, there is the CaF_2 structural type: FeS_2, $PtAs_2$, FeSAs.

The compounds with atomic lattices are very hard (SiC, diamond) and have a very high melting point and mechanical resistance.

The unit cell of diamond





2.Ionic Lattices

The ions are distributed alternatively as charges.

Take for instance the NaCl structure. NaCl should crystallize in a cubic closest packed array of Cl^- ions with Na^+ ions in the octahedral holes between planes of Cl^- ions. We can translate this information into a unit–cell model for NaCl by

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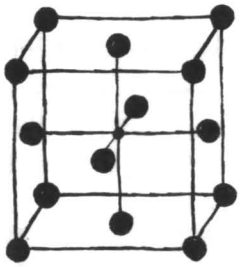
remembering that the face–centered cubic unit cell is the simplest repeating unit in a cubic closest–packed structure.

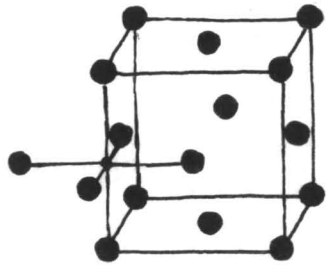
There are four unique positions in a face–centred cubic unit cell. The presence of a particle at one corner of the unit cell requires the presence of an equivalent particle on each of eight corners of the unit cell. There are also particles present on the center of faces.

The following figure (a) shows that there is an octahedral hole in the center of a face–centred cubic unit cell. Any particle at this point touches the particles in the centers of the six faces of the unit cell. Figure (b) shows the other octahedral holes in a face–centred cubic unit cell on the edges of the cell.

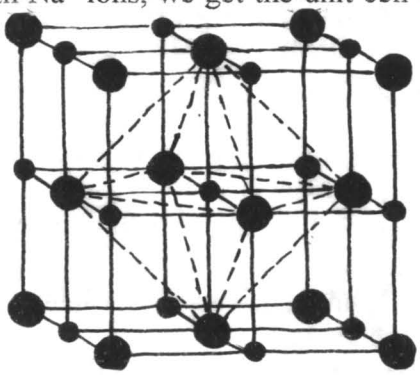
(a)



(b)



If Cl^- ions occupy the lattice points of a face–centred cubic unit cell and all of the octahedral holes are filled with Na^+ ions, we get the unit cell shown in the figure below:



In conclusion, NaCl crystallizes in a cubic unit cell. The cell–edge length is 0.5641 nm. Placing a Cl^- ion at these four positions implies the presence of a Cl^- ion on each of the 14 lattice points that define a face–centred cubic unit. Placing a Na^+ ion in the center of the unit cell and on the three unique edges of the unit cell requires an equivalent Na^+ ion in every octahedral hole in the unit cell.

ZnS crystallized as cubic closed–packed array of S^{2-} ions with Zn^{2+} ions in tetrahedral holes. The S^{2-} ions in this crystal occupy the same positions as the Cl^- ions in NaCl. The only difference between these crystals is the location of the positive ions. The figure below shows that the tetrahedral holes in a face–centered cubic unit cell are in the corners of the unit cell. An atom with these particles would touch the atom at this corner as well as the atoms in the centers of the three faces that form this corner. Although it is difficult to see without a three dimensional model, the four atoms that surround this hole are arranged toward the corners of a tetrahedron.

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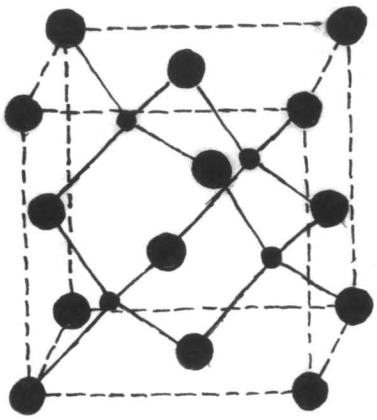

Zinc blende (cubic ZnS)

Because the corners of a cubic unit cell are identical, there must be a tetrahedral hole in each of the eight corners of the face–centered cubic unit cell. If S^{2-} ions occupy the lattice points of a face–centered cubic unit cell and Zn^{2+} ions are packed into every other tetrahedral hole, we get the unit cell of ZnS.

In conclusion, it can be said that ZnS crystallizes in a cubic unit cell. The cell–edge length is 0.5411 nm.

It can be observed that only half of the tetrahedral holes are occupied in this crystal because there are two tetrahedral holes for every S^{2-} ion in a closest–packed array of these ions.

The ionic lattices can be separated into:

–simple ionic lattices

—if the unit cell is simply cubic, the coordination number is 8, CsI is the structural type. For example: CsBr, RbF, TlCl, TlBr, TlI, NH_4Cl, NH_4Br

CsCl (α) structure has the CsI structure and at 460^0C it turns into CsCl (β) with the structure like NaCl.

—if the unit cell is face centered cubic and the C.N. = 6 (alkaline halides):

AB type. NaCl structural type: AgCl, AgBr, MgO, CaO, CaS, CdO, PbS, NiO.

AB_2 type: C.N. = 4: CaF_2 structural type: BaF_2, SrF_2, CdF_2, ZrO_2, CeO_2, ThO_2, LiO_2, Na_2S.

—sublattices: TiO_2 (Ti has the C.N. = 6 and O has the C.N. = 3) structural type: MgF_2, ZnF_2, NiF_2, MnO_2, PbO_2.

–complex ionic lattices

Complex ions are polyatomic ions like: SO_4^{2-}, CO_3^{2-}, $PtCl_6^{2-}$.

Because of the geometry of the complex ions (ex.: Td (SO_4^{2-}); D_{3h} (CO_3^{2-}); O_h ($PtCl_6^{2-}$)), the symmetry of the lattice is usually different from that of the simple ions. For instance: $CaCO_3$: the arrangement and the stoeichiometry is the same with NaCl (f.c.c.) but the plane CO_3^{2-} distorts the cube in a triclinic system.

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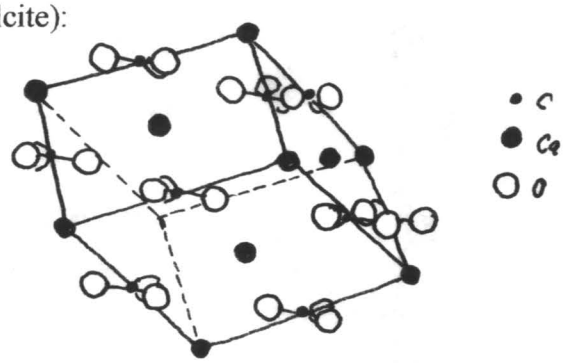
The unit cell of $CaCO_3$ (calcite):

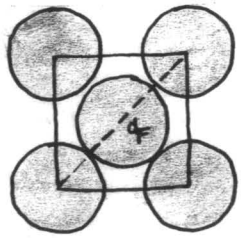


Calculating Metallic or Ionic Radii

Estimates of the radii of most metal atoms can be found.

Nickel crystallizes in a face–centred cubic unit cell with a cell–edge length of 0.3524 nm to calculate the radius of a nickel atom.

One of the faces of a face centred cubic unit cell is shown in the figure below:



According to this figure, the diagonal across the face of this unit cell is equal to four times the radius of a nickel atom

$$d_{face} = 4\ r_{Ni}$$

The Pythagorean theorem states that the diagonal across a right triangle is equal to the sum of the squares of the other sides. The diagonal across the face of the unit cell is therefore related to the unit–cell edge length by.

$$d_{face}^2 = a^2 + a^2 \Rightarrow d_{face} = \sqrt{2}\ a$$

$$4\ r_{Ni} = \sqrt{2}\ a$$

Solving for the radius of a nickel atom gives a value of 0.1246 nm:

$$r_{Ni} = \frac{\sqrt{2}\ a}{4} = \frac{\sqrt{2}\ (0.3524\ nm)}{4} = 0.1246\ nm$$

A similar approach can be taken to estimating the size of an ion. Let's start by using the fact that the cell–edge length in cesium chloride is 0.4123 nm to calculate the distance between the centers of the Cs^+ and Cl^- ions in CsCl.

CsCl crystallizes in a simple cubic unit cell of Cl^- ions with a Cs^+ ion in the center of the body of the cell, as shown in the figure:

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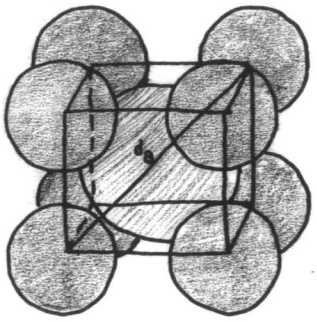

Before we can calculate the distance between the centers of the Cs^+ and Cl^- ions in this crystal, however, we must recognize the validity of one of the simplest assumptions about ionic solids: the positive and negative ions that form these crystals touch.

We can therefore assume that the diagonal across the body of the CsCl unit cell is equivalent to the sum of the radii of two Cl^- ions and two Cs^+ ions.

$$d_{body} = 2\, r_{Cs^+} + 2\, r_{Cl^-}$$

The three–dimensional equivalent of the Pythagorean theorem suggests that the square of the diagonal across the body of a cube is the sum of the squares of the three sides.

$$d_{body}^2 = a^2 + a^2 + a^2 \Rightarrow d_{body} = \sqrt{3}\, a$$

$$d_{body} = \sqrt{3}\, a = \sqrt{3}\,(0.4123 \text{ nm}) =$$

$$= 0.7141 \text{ nm}$$

The sum of the ionic radii of Cs^+ and Cl^- ions is half this distance:

$$r_{Cs^+} + r_{Cl^-} = d_{body} / 2 = 0.3571 \text{ nm}$$

If we want to estimate the size of either the Cs^+ or Cl^- ion, we could use the results to calculate the radius of the other ion. The ionic radius of the Cl^- ion is 0.181 nm. Substituting this value into the last equation gives a value of 0.176 nm for the radius of Cs^+ ion.

$$r_{Cs^+} + r_{Cl^-} = 0.3571 \text{ nm}$$

$$r_{Cs^+} + 0.181 \text{ nm} = 0.3571 \text{ nm}$$

$$r_{Cs^+} = 0.176 \text{ nm}$$

The results of this calculation are in reasonable agreement with the value of 0.169 nm known for the radius of the Cs^+ ion. The discrepancy between thesis values reflects the fact that ionic radii vary from one crystal to another. The tabulated values are averages of the results of a number of calculations of this type.

3.Molecular Lattices

Molecular lattices present substances composed by covalent molecules held in a crystal by weak van der Waals forces.

The simplest lattices are those of the rare gases (molecules of the type X – composed of a single atom). Except helium that crystallises in a hexagonal compact lattice, all the rare gases crystallise in cubic face centred cubic lattices:

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f.c.c.: Ne, Ar, Xe, Kr – dispersion forces;

I_2, CO_2 – van der Waals induced forces;

H_2O, uree – Hydrogen bonds.

Covalent rays of atoms were determined by the X–rays method applied to molecular crystals.

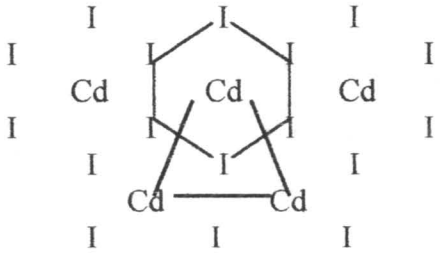
4.Layer Lattices

The layers are composed by ions or atoms, with ionic or covalent interaction and between layers there are van der Waals forces, Hydrogen bonds.

The nature of particles divided the layer lattices into:

(i) ionic layer lattice: CdI_2

Each Cd^{2+} is octahedral surrounded by 6 ions of I^-. Each I^- has three Cd^{2+} as neighbors . The ratio of the cadmium ions and the chloride ions is of 1 : 2 and corresponds to the formula CdI_2. One plane is formed by a cleavage plane composed by a triple layer of ions: two planes of ions in exterior and a Cd ion between them.



The CdI_2 crystal s composed by this kind of triple, infinite layers parallel orientated. In crystal are set planes of chloride that are attracted only by van der Waals forces. These planes coincide with the cleavage planes.

Example of lattices with CdI_2 structural type:

AB_2 type: halides like MgI_2, CaI_2, PbI_2, MnI_2, FeI_2, $MgBr_2$...

sulfides like MS_2 (M – metal)

selenides like MSe_2 (M – metal)

hydroxides like $Mg(OH)_2$ and $Ca(OH)_2$.

In the crystals with CdI_2 lattice, the successive layers are set in such a way that they give a hexagonal or a cubic symmetry to the crystal.

(ii) the atomic layer lattice: graphite

Is one of the crystalline forms of carbon and is composed by parallel planes of carbon. In these planes, there are regular hexagons with the edge of 1.415 Å. Each atom has three neighbors and the bonds between atoms are of 120^0. This is a planar arrangement of sp^2 hybridized carbon. So there is an extended π orbital over the whole plane of one layer of carbon atoms. This explains the good electrical conductivity of graphite, its dark color, good thermal conductivity and the easy cleavage of the crystal in a parallel direction with the atom planes. The atomic planes are bounded only by weak van der Waals bonds.

There in known only one compound that crystallizes with the graphite lattice: BN, boron nitride.

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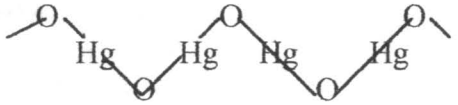
Another type of layer lattice is the catenar lattice. This kind of lattice is composed by infinite chains of atoms. For instance: plastic sulph and glass selenium.

HgO crystallizes in two forms: – a rhombic one, more usual, of infinite chains



– a hexagonal one, of similar chains but under the helix form

Isomorphism and Polymorphism

• Substances with similar formulas often crystallize in identical crystalline forms. Those substances are called isomorphic (Mitscherlich, 1818). Substances like $CaCO_3$ and $NaNO_3$ are isomorphic, without being chemically related. Some crystallize with different rays:

$SO_4^{2-} \cdot 7\ H_2O$ – in monoclinic systems, crystallize with:

Mg^{2+}	Fe^{2+}	Ni^{2+}
0.65 Å	0.75 Å	0.69 Å

Isomorphic substances that crystallize in the tetrahedral form are:

MnO_4^- ClO_4^- BF_4^- SO_4^{2-}

A characteristic property of the isomorphic solid substances is that they form mix crystals also called solid solutions. Two substances with similar lattices (ionic, atomic or molecular) can form (after melting or fusion) unity crystals. For instance: KCl and KBr can form mix crystals.

• Polymorphism is the property of the same substance to crystallize in more then one crystalline system. It can be encountered at many substances. For instance, at carbon: diamond (crystal in the cubic system) and graphite (hexagonal system);
ZnS, zinc sulfide: blende (cubic) and wutrzite (hexagonal);
$CaCO_3$: aragonite and calcite.
At the crystallization of a substance, the less stable form is first obtained.
There are two kinds of polymorph transformations:

1.irreversible or monotropic when the unstable form passes irreversible in the stable form:

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–diamond passes, under the action of temperature and in a long time in the absence of air, in graphite.

–SiO_2 (quartz) passes in tridimite and then in cristabalit.

2.reversible or enantiotropic when each form is stable in a range of temperature:

–S orthorhombic ☐ S monoclinic and reverse when the temperature reaches the limit of 95^0.

–α–CsCl (s.c.c.) ☐ β–CsCl (f.c.c.) at 460^0

Generally, the polymorphism is found for metals (α, β, γ, ...) where α form is the stable form.

For the simple substances, the polymorphism property is called allotropy:

O_2 / O_3;
S_2 / S_4 / S_8;
diamond / graphite;
P_4 white / red...

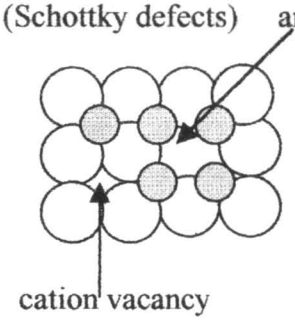
Real and Ideal Crystals

An ordered lattice, perfectly organized is an ideal lattice. Practically, solids are not perfectly organized and are called defects of the lattice.

Imperfections in crystals arise from dislocation of ions, ion vacancies in the lattice or nonstoeciometric ratio or by the presence of foreign ions or impurities in the lattice.

There are two types of defects:

a) Schottky defects: vacancies of anions and cations which are equal in number (Schottky defects)



b) Frenkel defects: occur when an ion occupies an interstitial site, leaving its normal site vacant. These defects are more likely in crystals in which the anion and cation differ greatly in size so that the smaller ion can fit into the interstitial site. Example: AgBr.

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5.Metallic Lattices

Metals crystallize in the compact lattices that correspond to body centered (C.N. = 8) corresponding to CsCl structure, face centered cubic (f.c.c., corresponding to NaCl, C.N. = 12) or hexagonal system (C.N. = 12):

f.c.c.: Cu, Ag, Pt, Pd, Pb, Al, Ni, Fe;
b.c.c.: Ba, Cr, Fe, W, V, alkaline metals;
hexagonal: Be, Mg, Zn, Cd.

With such great coordination numbers for each atom, we immediately encounter great difficulty in proposing a stereo–related bonding model for metals according to the covalent, electron pair concept.

In many ways, the most successful model of the electronic structure of metals (but this model is not practically useful with regard to lattice structure) is an extended form of molecular orbital theory that deals with physical properties of metals such as electrical conductivity. The theory is known as the band theory of metals.

Within limits, the great overlap between orbitals, the greater the energy gap between bonding and antibonding orbitals. Applying this idea to a crystal of a metallic element (a "molecule" of an infinite number of atoms) we are confronted with so many lattice orbitals that the band of orbitals energies for the valance electrons of the metal atoms approach a continuum.

Photoelectric materials fit into this model as cases for which the gap between a filled valance band and empty valance band is comparable to visible / ultraviolet photon energies. Here, electronic absorption causes both higher and lower bands to be partially filled.

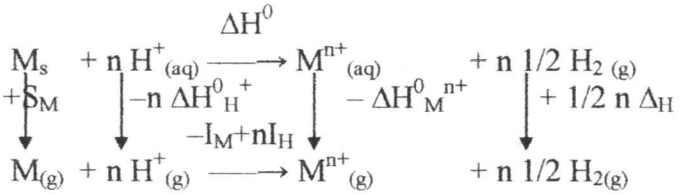
Another optical property of metals that fits into this model is their high reflectivity or luster.

"Doping" semiconductors with elements having fewer or greater number of valance electrons than possesses the semiconductor atoms can control the semiconductor properties of many materials. Doped semiconductors are distinguished by the term "extrinsic".

Oxidative Stability

One of the most interesting aspects of the chemistry of metals and in the same time most difficult to understand is their oxidation potential.

In an attempt to identify factors that influence the activities of these elements, we may use a Born–Haber cycle for the reaction of the elemental metal with aqueous H^+ (H_3O^+).



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– the difference $\chi_A - \chi_B$ is a measure of the distortion of the covalence between A–B.

The electronegativity of an atom has a constant value and depends on the nature of the bond, its oxidation state, the type of hybridization.

- The electronegativity increases when the oxidation state increases;
- The elecronegativity increases when the coordination number of the donor atom increases and it decreases when the coordination number of the acceptor atom increases.

Standard: $\chi_{Li} = 1$.

(b) Mulliken Method

One of the more important uses of the atomic terms energies have is the definition of the electronegativity.

The original ideas were advanced by Mulliken and more recently applied by Hinze and Jaffe.

Mulliken began with the definition of electronegativity by considering electron transfer between two atoms A and B:

$$A^-B^+ \leftrightarrow A^+B^-$$

If the electronegativities of A and B are identical, the two ionic pairs would have the same energy.

$E_{A^-B^+}$: depends on

the ionization energy of B: I_B: $B \rightarrow B^+ + e^-$ and

the electron affinity of A: E_A: $A^- \rightarrow A + e^- \Rightarrow -E_A$: $A + e^- \rightarrow A^-$

$$E^{(1)} = I_B - E_A$$

$E_{A^+B^-}$: depends on

the ionization energy of A: I_A: $A \rightarrow A^+ + e^-$ and

the electron affinity of B: E_B: $B^- \rightarrow B + e^- \Rightarrow -E_B$: $B + e^- \rightarrow B^-$

$$E^{(2)} = I_A - E_B$$

$$E^{(1)} = E^{(2)}$$

$$I_B - E_A = I_A - E_B$$

$$I_B + E_B = I_A + E_A$$

If A is more electronegative then B: $I_A + E_A > I_B + E_B$

In this situation, we must calculate the energy of the atom A in its ground state as an average of all terms, then the energy of A^+ and A^- as an average of all terms too.

Ground state energy:

$C\ (ns^2\ np^2)$ $\quad E = 1/15\ [\ 1 \cdot E(^1S) + 5 \cdot E(^1D) + 9 \cdot E(^3P)]$

$C^-\ (ns^2\ np^3)$ $\quad E = 1/20\ [\ 4 \cdot E(^4S) + 6 \cdot E(^2P) + 10 \cdot E(^2D)]$

$C^+\ (ns^2\ np^1)$ $\quad E = 1/6\ [\ 6 \cdot E(^2P_{1/2})]$

Thus the electronegativities are different for an orbital 2S and 2P, orbital electronegativities vary with the type of hybrid and the relative S and P character of the hybrid.

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In terms of enthalpies for the various steps we may write as an approximation for the enthalpy of the reaction of the metal with hydrogen ion:

$$\Delta H^0 = \Delta H^0_{M^{n+}} - 1/2\ n\ \Delta_H + S_M - n\ \Delta H^0_{H^+} + I_M - nI_H$$

$$\Delta H^0 = (S_M - 1/2\ n\ \Delta_H) + (I_M - nI_H) + (\Delta H^0_{M^{n+}} + n\ \Delta H^0_{H^+})$$

				$\sum$	E^0_{abs}
Li	–0.63	–8.21	+5.84	–3.0	+3.0
Na	–1.11	–8.46	+6.97	–2.6	+2.7
K	–1.31	–9.26	+7.84	–2.7	+2.9
Rb	–1.31	–9.42	+8.14	–2.6	+2.9
Cs	–1.42	–9.71	+8.44	–2.7	+2.9
Be	–0.58	+0.15	+1.22	–1.6	+1.9
Mg	–1.46	–2.3	+1.08	–2.7	+2.4
Ca	–1.24	–4.6	+2.88	–3.0	+2.9
Sr	–1.39	–5.25	+3.58	–3.0	+2.9
Ba	–1.33	–6.0	+4.33	–3.0	+2.9
Al	–1.14	+4.17	–5.05	–2.0	+1.7
Ga	–1.27	+5.5	–5.09	–0.9	+0.5
In	–1.41	+4.0	–3.22	–0.7	+0.3
Tl	–1.64	+5.2	–3.05	+0.5	–0.7

It can be observed that Li is slightly more reactive than the other alkali metals, Be is the least reactive of the alkaline earth which tend to increase in reactivity with increasing of the atomic number. The reactivity of the group III A metals trend to decrease drastically with atomic number.

If:

$$\Delta G = - n\ F\ E^0,$$

then the reaction with the most positive E^0 is the most thermodynamically spontaneous one.

Among the alkali metals, the reactivity of Li in comparison with Na and the other members of the group can be based on the solvation energy of Li^+. The reactivity of Be seems to be due to a combination of high sublimation and ionization energies, as the solvation energy seems to play a less important role that it does for Li.

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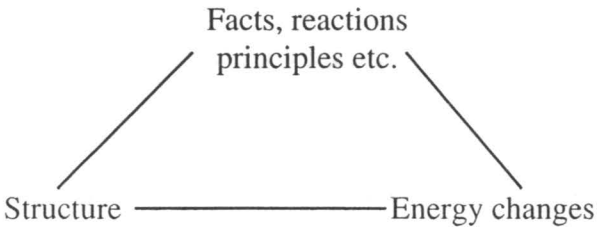
CHAPTER IX

ENERGETICS

IX.1. Introduction

At O level a study of chemistry can be summarized by the following triangle.



The emphasis at O level must be towards the learning of fact, principles, and reactions, with structure and energy changes being less important. The extent to which structure and energy changes are introduced varies from one syllabus to another.

For example, the melting of ice to give water is a simple process and a straightforward topic, which O level candidates should know. As an A level candidate you should appreciate that ice has an open crystal lattice with a tetrahedral structure. On heating, the water molecules in the lattice vibrate more and the structure breaks up on melting. The process requires energy:

$$e.g.\ \text{ice} + \text{energy} \rightarrow \text{liquid water}$$

This is an **endothermic** process and the energy required is called the **enthalpy change of fusion**.

You should always consider changes of structure and energy changes when answering questions. Nearly, all chemical reactions involve energy changes and study of energy changes is called **energetics**.

IX.2. First law of thermodynamics

This law is equivalent of the law of conservation of energy. It states that **energy cannot be created or destroyed but may be converted from one form into another**

$$q = \Delta U + w$$

where ΔU is the change in the internal energy

q is the actual heat change, and

w is the work done by the system.

The term w involves the gas produced expanding and pushing back the atmosphere. This can be estimated by using a syringe with a piston. The work done

$w = P\Delta V$ where P is external pressure and ΔV is the change in volume.

$P\Delta V$ (and hence w) only becomes significant when either P and/or ΔV is large. In reactions involving only solids and liquids as reactants and products $P\Delta V$ is negligible. For gases ΔV is frequently large and w can be significant.

Reactions carried out at constant volume. In these cases $\Delta V = 0$ (*i.e.* no change in volume) and $P\Delta V = w = 0$

$$q_v = \Delta U$$

q_v represents heat change at constant volume. Any heat change recorded corresponds to a change in the internal energy of the system.

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Reactions carried out at constant pressure. Most reactions carried out in the laboratory are carried out at constant pressure *e.g.* in an open beaker. Work is done by any gas expanding against the pressure of the atmosphere.

$q_v = \Delta U + P\Delta V$ where q_v represents the heat change at constant pressure

$$q_v = (U_{final} - U_{initial}) + P(V_{final} - V_{initial})$$

$$(U_{final} + PV_{final})\ (U_{initial} + PV_{initial})$$

The term $U + PV$ represents the energy possessed by the system and is called the **enthalpy** or **heat content** H:

$$q_v = H_{final} - H_{initial} = \Delta H$$

Substituting,

$$\Delta H = \Delta U + P\Delta V$$

IX.3. Enthalpy change of reaction

The equation for the reaction between carbon and excess oxygen is

$$C_{(graphite)} + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.5 \text{ kJ mol}^{-1}$$

(Note mol^{-1} means per quantity shown in the equation *not* per mole of product.)

The combustion of 12g of graphite in excess oxygen liberates 393.5 kJ. (The negative sign for ΔH, by convention, tells us that energy is **liberated** or the reaction is **exothermic**).

The quantity of energy liberated or absorbed is given by the equation, ΔH is called the **enthalpy change of reaction**. Often standard enthalpy changes are quoted. These are the enthalpy changes at standard atmospheric pressure and at constant temperature, usually 25°C (or 298 K). The reactants and products are in their usual or standard states at 25°C. Carbon is in the form of graphite and oxygen and carbon dioxide are gases. The standard enthalpy change of reaction is represented by $\Delta H°$. If solutions are used they must have a concentration of 1 mol dm^{-3}.

It is impossible to estimate absolute enthalpies but only enthalpy changes. Elements in their standard states are regarded as having zero enthalpy.

There are a number of standard enthalpy changes, which are important and should be clearly defined.

IX.4. Standard enthalpy change of formation

The standard enthalpy changes of formation of a compound is the energy given out or taken in when one mole of the compound is formed from its constituent elements in their standard states at 25°C.

For example, $\Delta H_f^0 = -393.5 \text{ kJ mol}^{-1}$ for the formation of carbon dioxide.

IX.5. Standard enthalpy change of combustion

The standard enthalpy changes of combustion of a substance ΔH_c^0 are the enthalpy change when one mole of the substance in its standard state undergoes complete combustion.

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If the compound contains carbon, hydrogen and oxygen, the complete combustion will produce carbon dioxide and water.

$$e.g.\ C_2H_6(g) + 3\tfrac{1}{2}\,O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H_c^0 = -1560\ \text{kJ mol}^{-1}.$$

In any chemical reaction the change of the enthalpy is:

$$aA + bB \rightarrow cC + dD$$

$$\Delta H = \Delta H_{products} - \Delta H_{reactants}$$

$$\Delta H = c\Delta H_C + d\Delta H_D - (a\Delta H_A + b\Delta H_B)$$

$$\Delta H = \Sigma n_p H_p - \Sigma n_r H_r$$

IX.6. Standard enthalpy change of neutralization

The standard enthalpy change of neutralization is the enthalpy change when 1 mole of H3O+ ions is just neutralized by an alkali in dilute solution. The acid and base are in their standard states at 25°C and the acid and base are in solution containing 1 mol dm^{-3}.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

$$\Delta H_c^0 = -57.1\ \text{kJ mol}^{-1}$$

The values obtained for standard enthalpy changes of neutralization of strong acids and strong bases are constant.

IX.7. Enthalpy change of solution and enthalpy change of dilution

The enthalpy change of solution is the enthalpy change when 1 mole of substance is dissolved in a specified volume of solvent. The enthalpy change will depend upon the volume of solvent used.

The enthalpy change of dilution is the enthalpy change when 1 mole of substance is dissolved in a large volume of solvent such that further dilution produces no further enthalpy change.

IX.8. Measuring enthalpy change

Enthalpy change is determined by simple calorimetric experiments. For example to determine the enthalpy change of neutralization of sodium hydroxide and hydrochloric acid, a known volume of sodium hydroxide solution of known concentration is placed in a vacuum flask and the temperature is accurately measured. The volume of hydrochloric acid, of known concentration, required to neutralize the sodium hydroxide solution is rapidly added, the mixture stirred and the final temperature recorded.

If the initial temperature of both the acid and alkali is t_1°C and the final temperature is t_2°C, the temperature change is $t_2 - t_1$°C. If the mass of the mixture is mg, the specific heat capacity of the solution is 4.2 J deg^{-1} (dilute solutions can be assumed to have the same specific heat capacity as water), and the heat capacity of the vacuum flask is W, then

$$\text{heat evolved} = m \times 4.2 \times (t_2 - t_1) + W \times (t_2 - t_1)\ \text{J}$$

From these results the enthalpy change of neutralization can be calculated.

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IX.9. Hess's law

Hess's law can be used for calculating enthalpy changes, which cannot be determined by experiment. the law states that the total enthalpy change for a reaction is independent of the route taken.

For example if X is converted to Y and Y to Z, the total enthalpy change will be the same as when X is converted directly to Z.

Example: Calculate the standard enthalpy change of formation of carbon monoxide from the following information:

Enthalpy changes of combustion of carbon (graphite) and carbon monoxide are -393.5 kJ mol^{-1} and -283 kJ mol^{-1}.

The following equation can be written

Required: Enthalpy change of formation of carbon monoxide

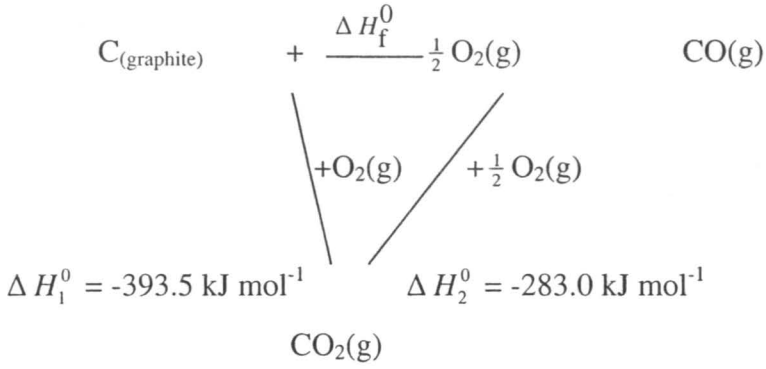
$$C(graphite) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g)$$

Given: Enthalpy change of combustion of graphite and carbon monoxide

(i) $C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^\circ = -393.5$ kJ

(ii) $CO(g) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^\circ = -283$ kJ

A diagram can be draw to summarize the situation



$$\Delta H_1^0 = \Delta H_1^0 - \Delta H_1^0 = -393.5 + 283.0 = -110.5 \text{ kJ mol}^{-1}$$

Alternatively, from equation *(i)* and *(ii)* above, equation *(ii)* can be reversed when the enthalpy change is the same numerically but the sign is changed.

$C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^\circ = -393.5$ kJ

$CO_2(g) \rightarrow CO(g) + \tfrac{1}{2} O_2(g)$ $\quad \Delta H^\circ = +283$ kJ

Adding these two equations together

$C(graphite) + \tfrac{1}{2} O_2(g) \rightarrow CO(g)$ $\quad \Delta H_f^0 = -393.5 + 283.0 = -110.5$ kJ mol^{-1}

The **negative** sign shows, by convention, that the process is **exothermic**. A **positive** sign shows that the process is **endothermic**. Candidate loses many marks in this type of work by either getting a sign wrong or by missing out units. It is advisable when an enthalpy change is positive

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to put in a positive sign. This shows the examiner that you have thought about it and decided that the process is endothermic.

IX.10. Bond enthalpies

During a chemical reaction a number of bonds will be formed or broken. **Forming bonds liberates energy and breaking bonds requires energy**. It would be useful to be able to attribute specific enthalpy changes to various bond changes. The sum of these enthalpy changes would equal the total enthalpy change.

Consider the breaking of the four C — H bonds in methane:

$$\begin{array}{c} H \\ | \\ H-C-H\,(g) \\ | \\ H \end{array} \rightarrow C(g) + 4H(g) \qquad \Delta H^\circ = -393.5 \text{ kJ mol}^{-1}$$

It is reasonable to assume that the energy required to break each C — H bond is the same and the same as is required to break a C — H bond in any other compound, and for all practical purposes this can be taken as true at this level.

For a diatomic molecule XY, the bond enthalpy is defined as the enthalpy change for the process:

$$X-Y(g) \rightarrow X(g) + Y(g)$$

Table IX.1 lists some of the average bond enthalpies at 25°C.

Table IX .1 - Some average bond enthalpy at 25°C

Bond	ΔH kJ mol^{-1}
H — H	+436
C — C	+348
C == C	+612
C — F	+484
C — Cl	+338
C — Br	+275
C — I	+238

It must be remembered these bond enthalpies can only be used as a guide. The actual value of a bond enthalpy will depend upon the nature of other atoms or groups joined to it.

The enthalpy change is positive when a bond is broken and negative on making a bond. Bond enthalpies can be used to explain a number of facts from inorganic and organic chemistry.

E.g. The increased reactivity of phosphorus compared with nitrogen or the increased rate of substitution reactions for iodoalkanes compared with other haloalkanes.

The enthalpy change for atomization can be estimated using bond enthalpies. for example, the atomization of ethane C_2H_6 involves the breaking of one C — C bond and six C — H bonds. The enthalpy atomization of there is:

$$= 1(C-C) + 6(C-H) = 348 + (6 \times 412) = +2820 \text{ kJ mol}^{-1}$$

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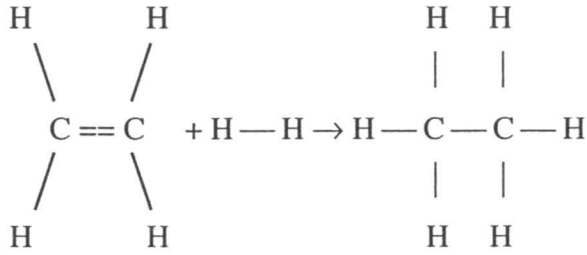
Bond enthalpies can also be used to estimate likely enthalpy changes in chemical reactions, *e.g.* the hydrogenation of ethane



Using the information in Table V.1

Bond broken 1(C — C) + 1(H — H) Enthalpy change = +612 +436 = +1048 kJ

Bond formed 1(C — C) + 2(C — H) Enthalpy change = -348 +2(-412) = -1172 kJ

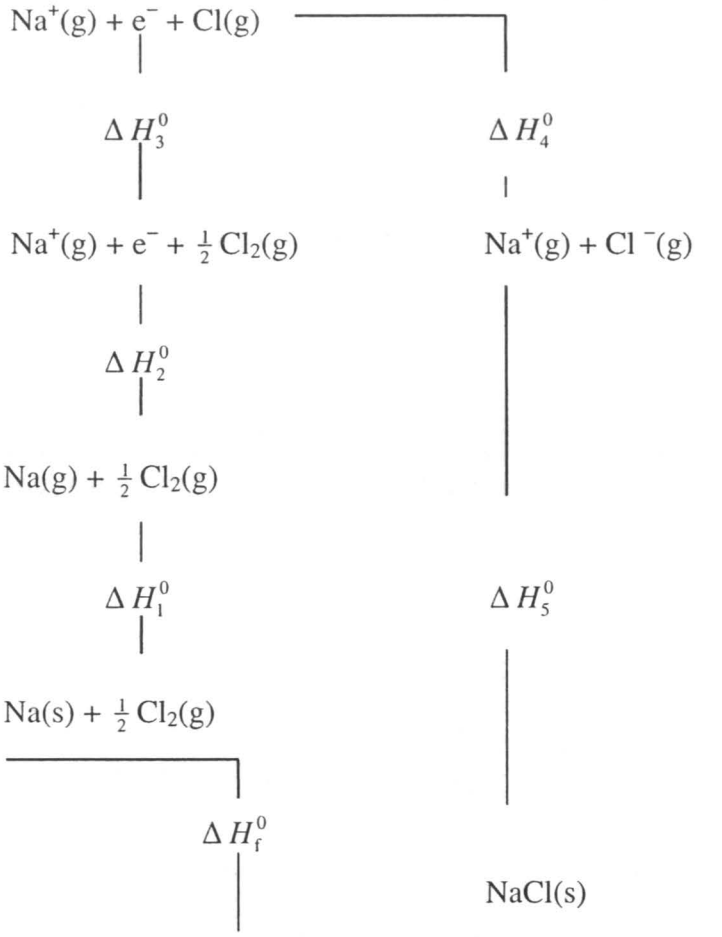
Net enthalpy change = 1048 - 1172 = -124 kJ

IX.11. Born-Haber cycle

Lattice enthalpies cannot be determined directly but may be found indirectly by using an **energy diagram**. These diagrams are called **Born-Haber cycles**. The most common one seen on examination papers is the one for sodium chloride.

The standard enthalpy change when one mole of sodium chloride crystal is produced from sodium metal and chlorine gas can be determined experimentally and is, in fact, the standard enthalpy change of formation of sodium chloride $\Delta H_f^0 = -411 \text{ kJ mol}^{-1}$.

We can consider the various steps, which are required to bring about this change:



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ΔH_1^0 corresponds to the **standard enthalpy change of atomization** of sodium. It is the enthalpy change when one mole of solid sodium is converted to free sodium atoms.

$$\Delta H_1^0 = +108.4 \text{ kJ mol}^{-1}$$

ΔH_2^0 corresponds to the **first ionization energy** of sodium *e.g.* the enthalpy change when one mole of electrons in their ground state is totally removed from 1 mole of sodium atoms in the gas phase.

$$\Delta H_2^0 = +500 \text{ kJ mol}^{-1}$$

ΔH_3^0 corresponds to the **standard enthalpy change of atomization** of chlorine. This is the enthalpy change when one mole of gaseous chlorine atoms is produced from chlorine molecules.

$$\Delta H_3^0 = +121 \text{ kJmol}^{-1}$$

ΔH_4^0 corresponds to the **first electron affinity** of chlorine. This is the enthalpy change when one mole of chlorine atoms each accepts one electron to form one mole of chlorine ions.

$$\Delta H_4^0 = -364 \text{ kJmol}^{-1}$$

ΔH_5^0 corresponds to the **lattice enthalpy** sometimes called **lattice energy**)of sodium chloride.

By Hess's Law $\Delta H_f^0 = \Delta H_1^0 + \Delta H_2^0 + \Delta H_3^0 + \Delta H_4^0 + \Delta H_5^0$

$$\Delta H_5^0 = -776.4 \text{ kJmol}^{-1}$$

An understanding of lattice enthalpy is extremely useful in various ways at A level:

(i) Substances with high lattice enthalpies will have melting points.

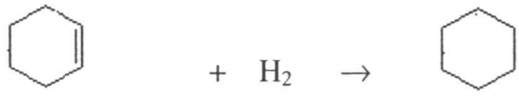
(ii) The solubility of an ionic compound will depend upon the relative values of the lattice and hydration enthalpies or energies.

(iii) Comparison of the calculated and experimental values lattice enthalpy gives an indication of the degree of covalent bonding in a compound.

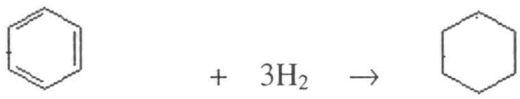
(iv) Lattice enthalpies can be used to explain the non-existence of some compounds.

IX.12. The stability of benzene

The enthalpy change of hydrogenation is the enthalpy change when one mole of hydrogen molecules is added to one mole of alkene. The enthalpy change of hydrogenation of cyclohexene is -120 kJ mol^{-1}.



If it is assumed that benzene contains three double bonds *i.e.* it is a triene, the enthalpy change of hydrogenation should be $3 \times (-120)$ kJ mol^{-1} *i.e.* -360 kJ mol^{-1}.



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The experimental value for the enthalpy change of hydrogenation of benzene is -208 kJ mol^{-1}. The difference between these two values (152 kJ mol^{-1}) is a measure of the extra stability of benzene compared with similar non-aromatic systems.

The standard enthalpy change of formation of benzene can be obtained by using the bond enthalpies in Table V.1 and assuming benzene is a cyclic triene.

$$\Delta H_f^0 = -(3 \times C{=}{=}C + 3 \times C{-}C + 6 \times C{-}H) = -5352 \text{ kJ mol}^{-1}$$

The experimental value found by a Hess's law calculation is -5549 kJ mol^{-1}. The difference between these two values (197 kJ mol^{-1}) again is a measure of the stability of benzene. The difference between this value and the one obtained previously from hydrogenation calculations is probably due to the use of average values for bond enthalpies.

IX.13. Second law of thermodynamics - entropy

The majority of reactions are exothermic and it was once believed that only exothermic reactions could take place. There is another factor, which governs the feasibility of a reaction.

The second factor is **entropy**, which is related to the degree of randomness or disorder in the system. If two gases in separate bulbs are allowed to come into contact, the gases mix and there is an increase in the disorder.

Given an opportunity, the disorder of a system, and hence its entropy, will spontaneously increase. The dissolving of an ionic crystal in water produces an increase in entropy. In the lattice the ions are regularly arranged. The dissolving of ammonium nitrate is an endothermic process and would not take place purely on energy considerations. There is, however, an increase in entropy, which makes the process possible.

One statement of the second law of thermodynamics is that in any system a change that takes place spontaneously (*i.e.* of its own accord) will always involve in a particular process divided by the temperature at which the process occurs *i.e.* $\Delta S = \frac{q}{T}$

Systems having perfect order *i.e.* the perfect ionic crystal lattice at 0 K, possess zero entropy. The entropy of a given mass of matter increases in the order:

$$\text{solid} \rightarrow \text{liquid} \rightarrow \text{gas}$$

The entropy of substances not possessing perfect order and of all substances at temperatures above 0 K will be greater than zero, *e.g.* the standard entropy S° (at 298 K and 1 atmosphere pressure) of water = 70 K^{-1} mol^{-1}.

The entropy change in a reaction can be found.

Example: Find ΔS° for the reaction

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

given that the standard entropies of hydrogen, gaseous iodine and hydrogen iodine are +131, +261 and +207 J mol^{-1} K^{-1} respectively.

$$\Delta S^\circ = 2 \times S^\circ_{HI} - S^\circ_{H_2} - S^\circ_{I_2} = 414 - 131 - 261 = +22 \text{ J mol}^{-1} \text{ K}^{-1}$$

There is an increase in entropy and a spontaneous reaction is feasible, although no indication is given of the possible rate of reaction.

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IX.14. Free energy *G*

This is a measure of the useful work, which can be obtained from a system (apart from volume changes).

A reaction can only proceed spontaneously ΔG is negative. ΔG depends upon ΔH and ΔS and they are related by the equation:

$$\Delta G = \Delta H - T\Delta S$$

Since for a reaction to proceed ΔG must be negative, for an endothermic reaction (ΔH positive), a reaction will take place only if $T\Delta S > \Delta H$. If ΔG is positive, no useful work can be obtained and the reaction is not feasible. If $\Delta G = 0$ the system will be in dynamic equilibrium.

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CHAPTER X

KINETICS AND EQUILIBRIUM

KINETICS

X.1. Introduction

Most O level courses now contain same work on rates of chemical reactions and the factors which affect the rate of reaction. The work on reaction kinetics becomes more significant at A level, because it is closely related to structure and to the mechanisms of reactions.

The factors, which can affect the rate of reaction, include:

(i) Physical state of reactants

(ii) Concentration (and gas pressure)

(iii) Temperature

(iv) Catalysts

(v) Light

These factors will be considered in turn.

X.2. Physical state of reactants

The reaction between calcium carbonate and dilute hydrochloric acid is

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

Figure X.1 shows the graphs that would be obtained if equal masses of powered calcium carbonate and lamps of calcium carbonate were reacted separately with equal volumes of dilute hydrochloric acid of the same concentration (and excess). The volume of carbon dioxide collected was measured at intervals.

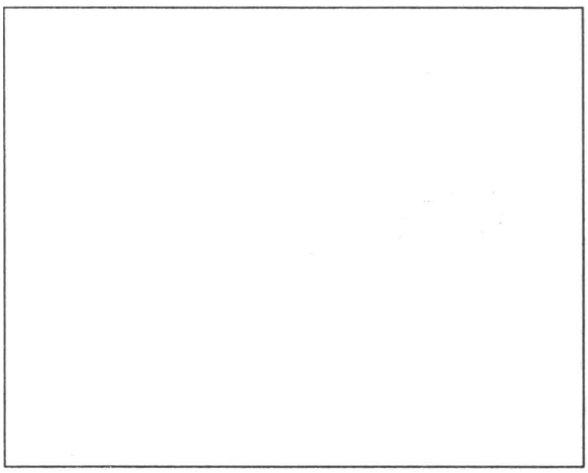

Figure X.1 - Effect of physical state on rate of reaction

The volume of carbon dioxide collected in each case is the same because equal masses of calcium carbonate were used. It is produced very quickly with the powder and more slowly with the lumps. The reaction with the powder is faster because the powder has a larger surface area and the reaction takes place when the acid comes in contact with the surface.

X.3. Concentration

This is probably the most important factor to understand at A level. During a reaction the reactants are used up and so the rate of reaction decreases.

The exact relationship between the rate of reaction and the concentration of the reactants in a particular reaction can only be determined experimentally. Most reactions take place in a series of steps and the rate of the overall reaction depends upon the rate of the slowest step, called the **rate determining step**.

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It is vital for you to distinguish clearly the meaning of the terms **order of reaction** and **molecularity**. Few candidates understand the distinction and many questions test this. The order of reaction is determined experimentally. In the reaction

$$A + B \rightarrow C + D$$

experiment may show that the rate of reaction is proportional to the concentration of A to the power of x

$$i.e.\ \text{rate} \propto [A]^x$$

and also the rate of reaction may also be proportional to the concentration of B to the power of y

$$i.e.\ \text{rate} \propto [B]^y$$

The overall equation is therefore

$$\text{rate} = k[A]^x\,[B]^y$$

k is the **rate constant** and the overall equation is called the **rate equation**. In this example, the order of the reaction with respect to A is x and order with respect to B is y and the total order of reaction is $x + y$.

In the reaction between peroxodisulphate and iodide ions, the equation is

$$S_2O_8^{2-}(aq) + 2\,I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$$

The rate equation determined experimentally is

$$\text{rate} = k[S_2O_8^{2-}]\,[I^-]$$

and the total order is 2. The order is not related to the equation. The order may be integral *i.e.* 1, 2 or 3 etc, but it can also be fractional.

$$e.g. \qquad H_2 + I_2 \rightarrow 2HI$$

$$\text{rate} = k[H_2]\,[I_2]$$

Order with respect to hydrogen = 1

Order with respect to iodine = 1

Total order of reaction = 1 + 1 = 2

$$H_2 + Br_2 \rightarrow 2HBr$$

$$\text{rate} = k[H_2]\,[Br_2]^{1/2}$$

Order with respect to hydrogen = 1

Order with respect to iodine = $\frac{1}{2}$

Total order of reaction = $1 + \frac{1}{2} = 1\frac{1}{2}$

X.4. Catalysts

A **catalyst** is a substance, which alters the rate of a chemical reaction without being used up. The catalyst may be changed physically but the mass of catalyst is unchanged at the end of the reaction.

An example of a catalyst is manganese(IV) oxide in the decomposition of hydrogen peroxide.

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

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This is an example of a catalyst, which speeds up a chemical reaction. A substance, which slows down the rate of a reaction, is called an inhibitor.

A catalyst does not alter the position of equilibrium or increase the yield of products. It merely alters the rate at which the equilibrium is achieved or the products are obtained. A catalyst provides an alternative route with a lower activation energy barrier for the reaction. More molecules possess the lower activation energy and so the reaction is speeded up.

e.g. $2HI \rightarrow H_2 + I_2$

Activation energy	without catalyst	183 kJ mol^{-1}
	with gold catalyst	105 kJ mol^{-1}
	with platinum catalyst	58 kJ mol^{-1}

There are two types of catalyst - **homogeneous catalysts** and **heterogeneous catalysts**. A homogeneous catalyst is in same phase as the reactants *e.g.* the reaction between an organic acid and an alcohol is catalyzed by the presence of hydrogen ion. A heterogeneous catalyst is not in same phase *e.g.* manganese(IV) oxide is solid and hydrogen peroxide is a liquid. There are two theories of catalysis.

1 Intermediate compound theory

The catalyst reacts with one of the reactants to produce an intermediate compound which eventually produces the required product and regenerates the catalyst, *e.g.* manganese(IV) oxide and hydrogen peroxide.

The intermediate compound theory explains most examples of homogeneous catalysis.

2 Adsorption theory

A gas is adsorbed when its particles collide with and adhere to the catalyst surface. When gas molecules are adsorbed they are brought close together, and in a state that enables them to react together. On desorption the catalyst surface is available for further reaction. An example is the reaction of an alkene with hydrogen using a nickel catalyst.

The *d*-block elements and their compounds are good catalysts. The elements can exist in a variety of oxidation states and the metal surfaces are ideal for adsorption purposes.

In same reactions one of the products of the reaction acts as a catalyst for the reaction. For example, in the reaction of an ethanedioate (oxalate) with acidified potassium manganate(VII), the reaction has to be heated to about 60°C to get the reaction to start but the manganese(II) ions produced catalyze the reaction and the reaction continues even if the solution is cooled to room temperature. This is an example of what is called **autocatalysis**.

X.5. Light

Some reactions are greatly affected by light. For example the reaction of hydrogen and chlorine is explosive in sunlight. The ultra violet light in sunlight splits some of the chlorine molecules into free chlorine atoms or chlorine **free radicals**.

$$Cl_2 \rightarrow 2Cl \bullet$$

Then a free radical chain reaction takes place producing hydrogen chloride.

$$Cl \bullet + H_2 \rightarrow HCl + H \bullet$$

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$$H\bullet + Cl_2 \rightarrow HCl + Cl\bullet$$

The reaction between chlorine and methane is another example of a reaction affected by light.

X.6. Methods of following the progress of a reaction

There are a number of methods, which can be used to follow the progress of a reaction. These include:

(i) Measuring the volume of gas evolved at intervals using a gas syringe, *e.g.* in the reaction between calcium carbonate and hydrochloric acid.

(ii) Measuring the electrical resistance of the solution.

(iii) Measuring the change color in the solution with a colorimeter.

(iv) Removing samples from the reacting mixture and titrating.

e.g. the hydrolysis of ethanoate with alkali. Portions of the reaction mixture are removed at intervals and titrated with dilute hydrochloric acid using phenolphthalein indicator.

EQUILIBRIUM

XI. Introduction

The topic of equilibrium is included in many O level syllabuses although many teachers leave it out or do not cover it adequately. It is an important topic at A level which needs to be understood before Units XI and XII are attempted.

X2. What is meant by chemical equilibrium?

The reaction between iron and steam is a reversible reaction

$$3Fe(s) + 4H_2O(g) \leftrightarrow Fe_3O_4(s) + 4H_2(g)$$

If steam is passed over heated iron in an open vessel, the forward reaction takes place and the iron oxide and hydrogen are produced. The steam displaces the hydrogen from the system, thereby limiting the reverse reaction.

When hydrogen is passed over the heated iron oxide, iron and steam are produced.

Equilibrium is established, however, if iron and steam are heated in a *closed* container so the products cannot escape. In equilibrium, the concentrations of the two products and the two reactants remain constant providing external conditions are unchanged. The reactions have not stopped however. The rate of the forward reaction is equal to the rate of the reverse reaction and so the concentrations are unchanged. Using the term **dynamic equilibrium** is probably better because it emphasizes the two reactions are continuing.

X3. Quantitive approach to equilibrium

The **law of mass action** states that, at constant temperature, the rate of a reaction is proportional to the active mass of the reacting substances. For A level purposes, active mass is the same as concentration in mol dm^{-3}. The law of mass action applies to an equilibrium in a homogeneous system. The sign $\leftrightarrow$ shows the system can reach equilibrium.

In the equilibrium

$$aA + bB \leftrightarrow cC + dD$$

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the equilibrium constant $K_c = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$ at constant temperature.

By convention, the concentrations of products are divided by reactants.

Equilibrium constants can be calculated using concentrations in mol dm^{-3}, and the equilibrium constant is represented by K_c . Partial pressures can also be used to calculate equilibrium constants and the equilibrium constant is then represented by K_p.

Example:

$$CH_3COOH(l) + C_2H_5OH(l) \leftrightarrow CH_3COOC_2H_5(l) + H_2O(l)$$

Calculate K_c in terms of *a,b* and *x* if *a* moles of ethanoic acid and *b* moles of ethanol are mixed and left reach equilibrium and *x* moles of ethanoic acid are used up.

$$CH_3COOH + C_2H_5OH \leftrightarrow CH_3COOC_2H_5 + H_2O$$

Initially	*a* moles	*b* moles	0	0
At equilibrium	(*a-x*) moles	(*b-x*) moles	*x* moles	*x* moles

In the total volume of the mixture is *V* dm^{-3}

$$[CH_3COOH] = \frac{a-x}{V} \qquad [C_2H_5OH] = \frac{b-x}{V} \qquad [CH_3COOC_2H_5] = \frac{x}{V} \qquad [H_2O] = \frac{x}{V}$$

(All units are mol dm^{-3})

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Substituting

$$K_c = \frac{\frac{x}{V}\times\frac{x}{V}}{\frac{(a-x)}{V}\times\frac{(b-x)}{V}} = \frac{x^2}{(a-x)(b-x)}$$

In this case, the volume of the mixture has no effect on the equilibrium constant.

If 1 mole of ethanoic acid and 1 mole of ethanol come to equilibrium, two third of mole of acid is used up. Calculate K_c .

$$\text{Substitute } a = 1 \text{ mole}, b = 1 \text{ mole}, x = \frac{2}{3} \text{ mole}$$

$$K_c = \frac{\frac{2}{3}\times\frac{2}{3}}{\frac{1}{3}\times\frac{1}{3}} = 4$$

The reactions involving gases, measuring the concentration at the same temperature are clearly different, although mathematically related. Just be consistent.

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X.4. Equilibrium in a heterogeneous system

The law of mass action can be modified to include heterogeneous systems. The common example is the heating of calcium carbonate in a closed system to prevent the escape of carbon dioxide

$$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$$

The vapor above the solid is a homogeneous system and

$$\frac{p_{CaO}}{p_{CaCO_3}} \times p_{CO_2} = \text{constant}$$

where p represents partial pressures. Thus at constant temperature the partial pressures of calcium carbonate and calcium oxide are constant. This is because the vapor pressures of solids are constant at constant temperature

$$K_p = p_{CO_2}$$

From this it follows that at any particular temperature, the partial pressure of carbon dioxide is constant.

X.5. Qualitative approach to equilibrium - Le Chatelier's principle

The way in which the position of equilibrium will change if one of the conditions is changed is predicted qualitatively using **Le Chatelier's principle**.

Le Chatelier's principle states that if one of the conditions is changed, the position of equilibrium will alter in such a way as to tend to restore the original conditions.

Consider the equilibrium

$$A + B \leftrightarrow C + D$$

At equilibrium A, B, C, and D are present, and the concentrations of these substances remains constant, providing conditions are unchanged. If the forward reaction is encouraged, a new equilibrium will be set up. In this equilibrium [C] and [D] will have increased and [A] and [B] will have decreased. The equilibrium is said to have 'moved to the right'.

A system 'moves to the left' if the new equilibrium established contains higher concentrations of A and B and lower concentrations of C and D.

The conditions, which are commonly changed, are:

(i) Concentrations of reactants or products.

(ii) Temperature.

(iii) Pressure. This is only important in reactions involving gases.

These conditions are considered separately.

Concentration

If the product C is removed by liquefaction, escape into the atmosphere etc, the reverse reaction cannot occur. The position of the equilibrium moves to the right. If the concentration of A and B is increased, again the forward reaction is encouraged and again the equilibrium moves to the right.

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Temperature

The change that takes place in equilibrium when temperature is altered depends upon whether the forward reaction is exothermic or endothermic (Figure X.1).

If the forward reaction is exothermic, the reverse reaction will be endothermic. The equilibrium can be written

$$A + B \leftrightarrow C + D \qquad \Delta H \text{ is negative}$$

If the temperature of the system is raised, the equilibrium moves to the left as the endothermic process will tend to reduce the temperature, *i.e.* restore the original conditions. Conversely if the temperature is decreased, the equilibrium moves to the right.

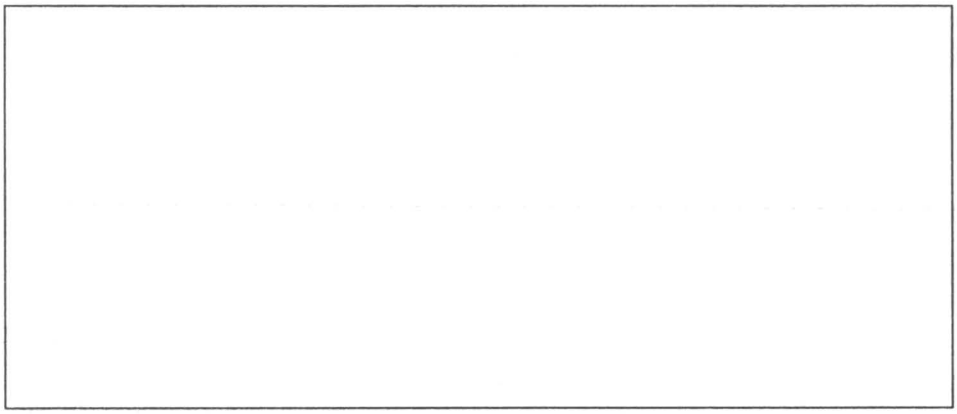

Figure X.1 - Energy changes in exothermic and endothermic reactions

Pressure

For a reaction involving gases, altering the pressure may cause a change in the position of the equilibrium.

For the reaction:

$$H_2(g) + I_2(g) \leftrightarrow 2HI(g)$$

at 700°C, the number of moles of reactants and products are the same. Pressure has no effect on the position of the equilibrium.

For a reaction where there is an increase in the number of moles from reactants to products, increasing the pressure moves the equilibrium to the left. Where there is a decrease in the number of moles from reactants to products, increasing the pressure moves the equilibrium to the right.

X.6. The Haber process for manufacturing ammonia

Ammonia is produced industrially from nitrogen and hydrogen.

$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

This reaction is reversible. The yield of ammonia will depend upon the conditions under which the reaction is carried out. If the optimum conditions are sought the best yield of ammonia for the cost will give the maximum profit.

Nitrogen is obtained by the fractional distillation of liquid air and hydrogen is obtained by the catalytic cracking of hydrocarbons or as a byproduct of the electrolysis of brine.

A mixture of nitrogen and hydrogen is dried and then compressed to 200 atmospheres. From the equation, and according to Le Chatelier's principle, the maximum yield of ammonia will be obtained by reducing the temperature. Unfortunately, lowering the temperature also decreases the rate of reaction and slows down the establishment of the equilibrium. The rate of the

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establishing the equilibrium can be increased by using a catalyst. Finely divided iron is used as a catalyst at approximately 500°C.

Under these conditions, only about ten per cent of nitrogen and hydrogen are converted to ammonia. The ammonia is removed from the gaseous mixture by cooling when the ammonia liquefies. The unreacted gases are recycled.

Much of the ammonia produced is subsequently converted to nitric acid or used to make ammonium compounds for fertilizers.

X.7. Contact process for manufacturing sulphuric acid

The Contact process involves three chemical reactions.

(i) Sulphur or a sulphur-containing mineral is burnt in air to produce sulphur dioxide.

$$S(s) + O_2(g) \leftrightarrow SO_2(g)$$

$$2ZnS(s) + 3O_2(g) \leftrightarrow 2ZnO(s) + 2SO_2(g)$$

or

(ii) The sulphur dioxide is reacted with further oxygen to produce sulphur(VI) oxide (sulphur trioxide).

$$2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g) \qquad \Delta H = -192 \text{ kJ mol}^{-1}$$

(iii) Sulphur trioxide is dissolved in concentrated sulphuric acid and the resulting solution is mixed with the correct quantity of water.

$$H_2SO_4(l) + SO_3(g) \leftrightarrow H_2S_2O_7(l)$$

$$H_2S_2O_7(l) + H_2O(l) \leftrightarrow 2H_2SO_4(l)$$

Only stage 2 is a reversible reaction so it is the conditions in stage 2 which will determine the final yield of sulphuric acid.

The forward reaction in Stage 2 is exothermic. According to Le Chatelier's principle, low temperatures will favor the maximum yield of sulphur trioxide. Again, lowering the temperature will slow the establishment of the equilibrium. A catalyst of vanadium(V) oxide is used to speed up the process and a compromise the temperature of 450 - 500°C is used.

In theory, the yield of sulphur(VI) oxide will be increased by increasing the pressure since there is a decrease in the number of molecules from left to right. In practice the extra yield obtained is so small that the extra cost could not be justified. The process is carried out at a little more than atmospheric pressure, to ensure a good flow of gas.

In the final stage the reaction of sulphur trioxide with water directly is too exothermic causing the acid to boil. The sulphur trioxide is dissolved in concentrated sulphuric acid to form oleum (or fuming sulphuric acid), which can be mixed with water to form concentrated sulphuric acid.

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